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 Hot Paper

When the Study of the Post-Synthetic Modification Method on a 1D Spin Crossover Coordination Polymer Highlights its Catalytic Activity

Yongjian Lai,^[a] Alejandro Enríquez-Cabrera,^[a] Alexia Ronci,^[a] Lionel Salmon,^[a] Lucie Routaboul,^{*[a]} and Azzedine Bousseksou^{*[a]}

We are interested in studying the catalytic activity of the spin crossover (SCO) complex $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$. In this work, we demonstrate that, by adapting the experimental conditions, we can switch from a quantitative post-synthetic modification (PSM) reaction to the use of this complex as a catalyst for the formation of imine from 4-amino-1,2,4-triazole. During the catalytic reaction, the iron complex undergoes two different PSM reactions: the first is the action of the aldehyde on the NH_2 groups present on the complex, whereas the second PSM reaction occurs between the imine complex and aminotriazole,


leading back to the starting complex. These two PSM reactions are at least partially involved in the catalytic mechanism. Furthermore, the combination of these two PSM reactions enables us to modulate the particle size and shape of the final amine complex without altering its excellent SCO properties. This result is of interest in the field of heterogeneous catalysis, where particle size has a strong influence on the catalytic activity, and for the proper integration in devices for different applications.


Introduction

For chemists, catalysis has always been an interesting field of research because of the possibility of synthesizing new molecules in a more efficient and faster way. For a long period of time, most catalysis has been performed with 4D and 5D metals, and within the last 30 years, research on first-row transition metals, including iron, has increased.^[1] The idea of using iron as a catalyst is appealing because it is cheap, abundant, biocompatible, and due to its electronic configuration, it is susceptible to spin crossover, which makes it attractive for spin catalysis.^[2] Spin crossover complexes (SCOs) are a specific type of phase change material that can reversibly switch around room temperature between a high spin (HS) state and a low spin (LS) state, with a concomitant well-known change in their physical properties (magnetic, electrical, optical, volume, etc.), and it has only recently been demonstrated its effect on their chemical reactivity,^[3] as we have recently shown.^[4] It is possible to incorporate them into different devices^[5] for photonics,^[6] electronics,^[7] thermal sensors^[8] and, more recently,

mechanical actuation.^[9] Among the different types of SCO complexes, we are interested in studying those from the family of 1D polymeric iron-triazole complexes, specifically $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ complex **1**, for which we have demonstrated that it is possible to modify the amino functionality quantitatively via PSM.^[10] We also studied the underlying mechanism of the PSM, where the solvent plays a key role.^[11] To the best of our knowledge, there is only one publication where these 1D triazole polymeric chain-like SCO complexes are used as catalysts, and the authors reported the use of this type of SCO in the oxidation of 3,4,5,6-tetrachlorocatechol (TCC) to the corresponding quinone in the presence of 3-chloroperbenzoic acid (CPBA). In fact, the active species is the oxidized SCO complex, which is formed by the reaction with CPBA, and once it is oxidized, it is later reduced by the TCC, regenerating the starting SCO.^[12] Therefore, in this case, the active catalyst is not the Fe^{II} complex but the oxidized species. Although they were able to observe a higher catalytic activity for the LS, this occurred because the rate-determining step is the oxidation of the SCO, which is more easily oxidized in the LS than in the HS. Even more generally, few synthesized complexes known for their spin crossover properties have been tested in catalysis.^[3,13] A priori, the design of spin crossover complexes is quite different from that of complexes used in catalysis. Indeed, in the former case, it is preferable that the ligands remain coordinated to the metal under various conditions to ensure the desired transition properties, whereas in the latter case, the presence of a hemilabile or easily substitutable ligand may be desirable so that the catalytic substrate can coordinate to the metal. However, it would be a disservice to stop at these apriori views, as the use of iron complexes in catalysis is currently attracting a great deal of interest due to the catalytic activity

[a] Y. Lai, A. Enríquez-Cabrera, A. Ronci, L. Salmon, L. Routaboul, A. Bousseksou CNRS, Laboratoire de Chimie de Coordination (LCC), 205 route de Narbonne, BP44099, Toulouse Cedex 4 31077, France
E-mail: lucie.routaboul@lcc-toulouse.fr
azzedine.bousseksou@lcc-toulouse.fr
Homepage: <https://www.lcc-toulouse.fr/en/switchable-molecular-materials-team-p/>

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and accessibility of iron complexes, as well as the environmental sustainability of iron complexes.^[14]

We have focused our attention in the $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ complex (complex 1, Figure 1), first because of its feasibility to quantitatively modify the amino functionality by PSM,^[10,11] and second because of its large thermal hysteresis loop above room temperature even when it is in suspension in ethanol, where both HS and LS can be found and studied at the same temperature.^[4] Owing to this hysteresis loop of the parent SCO complex, we can study the formation of the imine from the two spin states under strictly the same experimental conditions. We observed up to a 23% improvement in the efficiency of the PSM when going from the LS2 state to the HS state for complex 1.^[4] To the best of our knowledge, this is the first study in which the effect of the spin state on the organic reactivity of a functional group present on a metal complex has been reported.

In this manuscript, we present how, by carefully selecting the right conditions, we can proceed from performing a quantitative PSM reaction on the $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ complex by reacting with an aldehyde to the use of this complex to very effectively catalyze the formation of imine by adding only aminotriazole to the reaction. This is the first report in which the active species is indeed the SCO complex. In addition, experiments were carried out to determine the catalytic mechanism of this SCO iron complex.

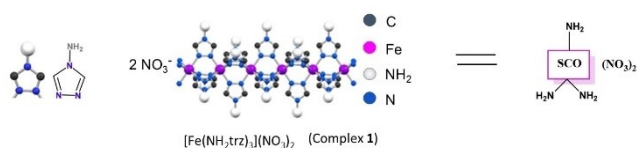


Figure 1. Chemical structure of complex 1 and its schematic representation used in this manuscript.

Results and Discussion

In the study carried out to demonstrate the effect of the spin state of iron on the efficiency of a PSM reaction on this coordination polymer, it was observed that the PSM reaction was quantitative at 1 h at 90 °C, whereas under the same experimental conditions, the reactions between 4-amino-1,2,4-triazole (a) (simply called aminotriazole in the rest of the manuscript) and *p*-anisaldehyde (b) led to the formation of only 10% (4-methoxybenzylidene)-4H-1,2,4-triazol-4-amine (hereafter referred to as imine c).^[4] We began the research described in this manuscript by studying the formation of imine functional groups under microwave irradiation (MWI). As shown in Figure 2a and 2b, microwave activation enabled us to obtain results in 10 minutes similar to those obtained in 1 hour in an oil bath thermostatted at 90 °C (see the ESI).

On the one hand, this result demonstrates that a reaction starting from an insoluble reagent (complex 1) is not systematically slower than a reaction where all the reagents are in solution. On the other hand, this result illustrates that coordination to a metal affects the organic reactivity of the ligand. Thus, combining the PSM method with a reaction, such as the digestion of the complex, which decoordinates the ligand from the iron, is also potentially interesting for the synthesis of new triazole-based organic molecules. This is interesting since triazole derivatives have many applications in the medical^[15] and materials^[16] fields.

To explain why these results are relevant, it is important to mention that since complex 1 is insoluble in ethanol and its compact molecular arrangement lacks apparent pores, some expected that the transformation of NH_2 groups on complex 1 took place in solution and not by the PSM reaction. A reaction pathway in solution automatically involves 3 steps (Figure 3): step A) decoordination of the ligand, leading to the presence of aminotriazole a in solution; step B) formation of imine c from amine a in solution; and step C) formation of complex 2. We

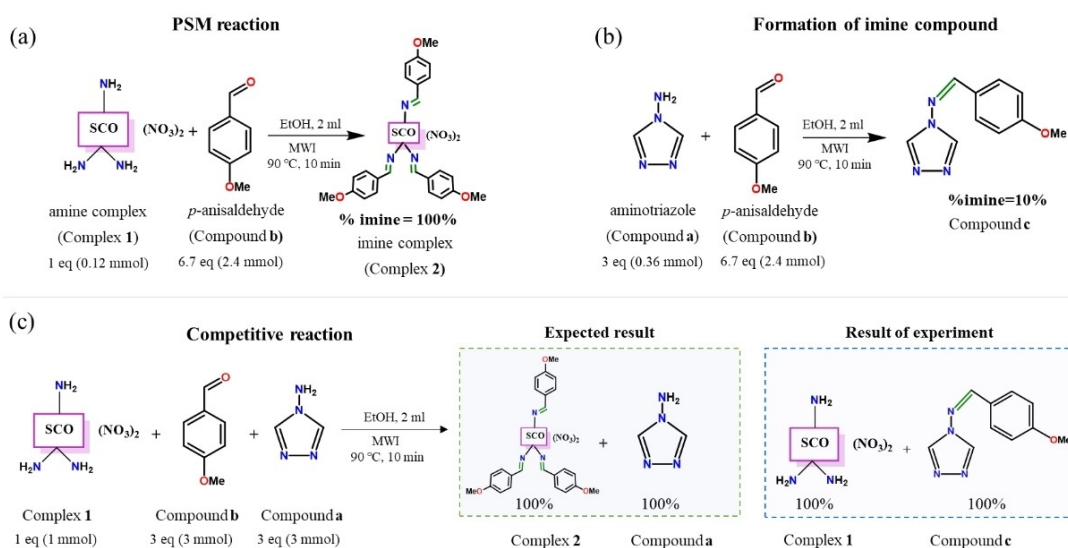


Figure 2. The reactions were carried out under microwave irradiation at 90 °C for 10 minutes. a) PSM reaction on complex 1 with aldehyde b; b) reaction between aminotriazole a and aldehyde b; c) competitive reaction in the presence of complex 1, amine a and aldehyde b.

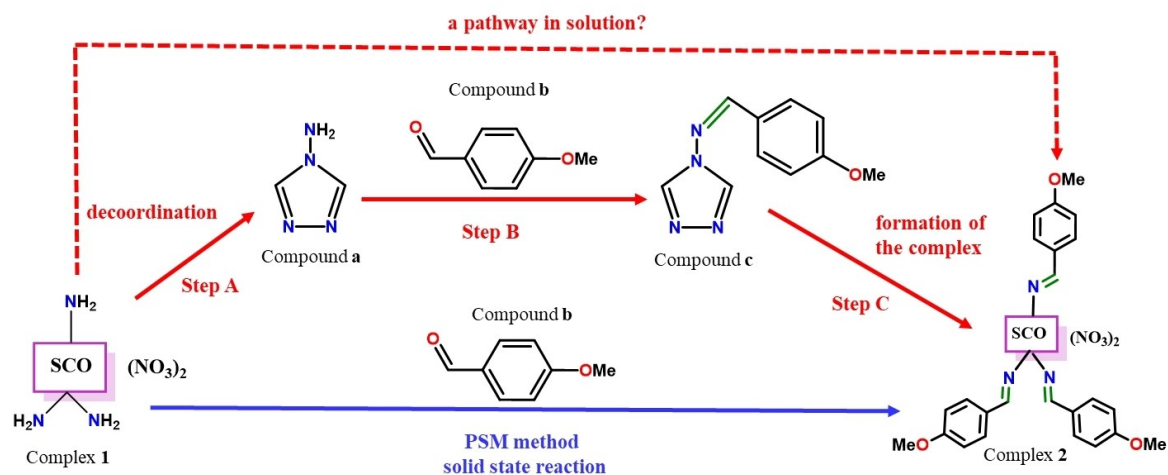


Figure 3. Reaction pathways envisaged for the formation of complex 2 from complex 1.^[11]

have previously demonstrated that the transformation in solution is unlikely, as steps A and C are not favored.^[11]

A further argument in favor of the transformation of the NH_2 groups present on the complex by the PSM reaction is the large difference in yields observed between the PSM reaction on the SCO complex and the reaction between aminotriazole **a** and *p*-anisaldehyde **b** in solution. Indeed, to obtain 100% imine on the complex, the formation of imine **c** in solution (step B) would have to be very fast, but the results in Figure 2a show that this is not the case since imine formation on the complex is much faster than that of the free ligand in solution (Figure 2b). To demonstrate that the amine complex **1** is more reactive toward aldehydes than the aminotriazole **a**, the competitive reaction shown in Figure 2c was tested. On the basis of the results of individual imine formation (Figure 2a and 2b), the quantitative formation of imine complex **2** was expected, whereas aminotriazole **a** should remain unchanged. In fact, the results obtained are the opposite of those we expected, as 100% of the aminotriazole **a** was transformed, and the recovered complex corresponds to amine complex **1**. As each type of experiment (individual reaction and competitive reaction) was repeated 3 times without any significant change in the results, we can consider the results to be reproducible and rule out the possibility that the difference in behavior observed between the individual reactions and the competitive reaction is due to experimental error. This surprising result seems to indicate that SCO catalyzes the formation of imine **c**. This is also a very interesting result since, to the best of our knowledge, it is the second example described in the literature where this family of complexes is used in catalysis.^[12] There is also no precedent in the literature where an iron complex is used as a catalyst for the reaction between aminotriazole **a** and an aldehyde. The closest example is the reaction between aminotriazole **a** and 9*H*-xanthen-9-ol, which is catalyzed by ferric hydrogenosulfate.^[17] In addition, imines synthesized from aminotriazole **a** are valuable compounds. These imines have potential applications in the medical field,^[18] and they are good ligands for a variety of metals.^[19] The complexes formed may

possess interesting properties or find applications in the medical^[20] or environmental^[21] fields.

The formation of imine **c** (Table 1) was subsequently tested in the presence of a catalytic amount of iron complex **1** (2.3% molar with respect to aminotriazole **a**). First, the formation of traces of acetal (generally approximately 2%) was observed. This side product is obtained by acetalization of aldehyde **b** in the presence of ethanol. Moreover, the presence of iron complex **1** in catalytic quantities greatly increases the imine yield (from 10% without catalyst to 40% with catalyst, Entries 1 and 2 of Table 1). The sonication of complex **1** in a suspension of ethanol for 10 min prior to the catalytic reaction resulted in a yield of 54% (Table 1, entry 3). This increase in yield can be

Table 1. The formation of the imine **c** catalyzed by iron complex **1**.

Conditions ^[a]		Yield	
Sonicate ^[b]	Heating ^[c]	imine	acetal
1	-	40%	2%
2	-	10% ^[e]	2%
3	10 min	54%	2%
4	10 min	58%	2%
5	10 min	> 98%	1%

[a] 20 mg of the complex was suspended in 0.5 mL of ethanol, two different solutions with a concentration of 4.1 mM of aldehyde (mixture 1) and 2 mM of aminotriazole (mixture 2) were prepared. [b] Sonication only the suspension of the complex at room temperature. [c] Heating the suspension of the complex at 90 °C under MWI. [d] 1 mL of mixture 1 was added to the complex in suspension, and it was heated at 90 °C under MWI. [e] Experiment done without complex

explained by improved access to the catalytic site.^[11] Complex 1 is insoluble in ethanol, and increasing the contact surface area of a heterogeneous catalyst increases its catalytic activity. The experimental conditions used to sonicate the suspension of complex 1 in ethanol do not reduce the particle size of complex 1, but they are sufficient to reduce the size of agglomerates. Entry 4 of Table 1 consists of heating a sonicated suspension of complex 1 in ethanol under microwave irradiation at 90 °C for 10 minutes, after which the aldehyde and aminotriazole were added to start the catalytic reaction. This heating could facilitate interactions between ethanol and complex 1 (greater diffusion of the solvent into the solid), leading to greater separation of the complex's polymeric chains. This better separation of the polymeric chains of complex 1 could, as observed during the study of the PSM method, lead to higher yields.^[11] Finally, imine **c** is obtained quantitatively when complex 1 is pre-treated (Table 1, entry 5). This pre-treatment consists of irradiating a reaction mixture of complex 1 and aldehyde in ethanol with microwaves for 10 minutes at 90 °C (Figure 4). However, what happens to complex 1 during pre-treatment and the catalytic reaction? At room temperature, the amine complex suspended in ethanol is pink. After microwave irradiation in the presence of the aldehyde and then return to room temperature, the complex became white (variable magnetic measurements of both complex 1 and 2 are provided in the ESI). This color change could indicate a modification in the chemical structure of the complex. This chemical modification was confirmed by IR spectroscopy, which revealed the appearance of bands characteristic of the C=N bond.

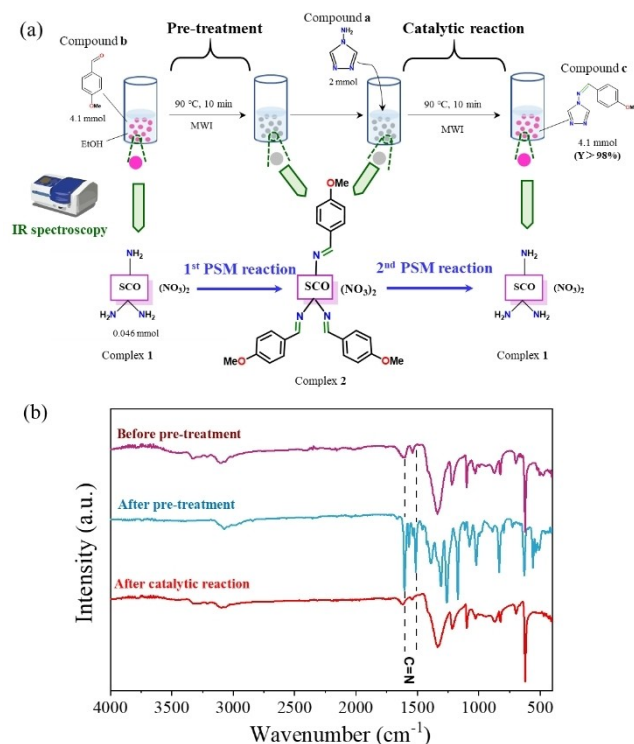


Figure 4. a) Schematic representation of the procedure where the pre-treatment is used in complex 1, where two consecutive PSM reactions occur. b) IR spectra of the recovered complex at each step.

After the catalytic reaction and return to room temperature, the complex returns to pink. IR spectroscopy of the complex after catalysis no longer shows the characteristic bands of the C=N functionality, and the IR spectrum corresponds to the amine complex. Therefore, during the pre-treatment and catalysis reactions, the amine complex undergoes two PSM reactions. The first PSM reaction occurs when the aminotriazole complex 1 reacts with the aldehyde to form the corresponding imine complex 2; only if aminotriazole **a** is present in solution, a second PSM reaction will occur between the aminotriazole **a** and the imine complex 2 to regenerate the starting complex 1 and leaving the imine ligand **c** in solution.

As we had previously demonstrated that the nature of the solvent strongly influenced the efficiency of the PSM method,^[11] we wished to study the effect of the solvent on the catalytic activity of the iron coordination polymer (Table 2).

Before discussing the various results obtained, it is important to note that a solution of aminotriazole in ethanol is systematically added to the iron complex suspension. We made this choice because aminotriazole is sparingly soluble in toluene, and the presence of ethanol keeps both reagents (aminotriazole and aldehyde) in solution. Entries 5, 10, and 15 of Table 2 correspond to the reactions performed without the complex. The best results are obtained when the amino complex is suspended in 96% ethanol while the other reagents are in absolute ethanol (see ESI); then, the amount of water present in the ethanol is also important.

This can be explained by the fact that the presence of a small amount of water in ethanol enhances the interaction between the solvent and the aminotriazole complex, which in turn results in even faster formation of the imine complex.^[11] Slightly better results are obtained when methanol is used as the solvent (Table 2, entries 6–10). This is to be expected, given that methanol, being more polar than ethanol, interacts even more strongly with the amine complex. When toluene is used as the solvent for suspending the complex and as the solvent for dissolving the aldehyde, poorer results are obtained compared with experiments carried out in methanol or ethanol (Table 2, entries 11–15). The presence of toluene could modify the interactions between the coordination polymer and the solvent, as well as the agglomeration of the particles of the complex. In the presence of toluene, pre-treatment appears to have a very limited effect on the yield of the catalytic reaction, in sharp contrast to the results obtained in ethanol or methanol. As expected, no formation of imine complex 2 was observed in toluene (see the ESI). When imine complex 2 is used in the ethanol-toluene mixture, 74% imine is obtained (Table 3, entry 12), whereas in ethanol, the imine is obtained quantitatively. This difference in yield could be explained by a slower PSM reaction or by less favorable contact between the imine complex and aminotriazole due to greater particle agglomeration.

The effect of the morphology of the catalyst was also investigated. If, as expected, amine complex particles catalyze imine formation, the use of smaller nanoparticles should be even more effective.

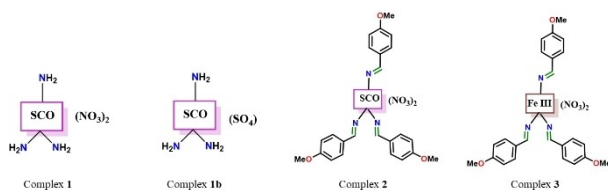
Table 2. Effect of the solvent on the efficiency of the catalytic reaction.

	Solvent		Conditions ^[a]			Yield
	Complex	Aldehyde	Sonicate ^[b]	Heating ^[c]	Pre-treatment ^[d]	
1	96 % EtOH	EtOH	-	-	-	40 %
2			10 min	-	-	54 %
3			10 min	10 min	-	58 %
4			10 min	-	10 min	100 %
5			-	-	-	10 % ^[e]
6	MeOH	MeOH	-	-	-	45 %
7			10 min	-	-	58 %
8			10 min	10 min	-	74 %
9			10 min	-	10 min	100 %
10			-	-	-	11 % ^[e]
11	Toluene	Toluene	-	-	-	33 %
12			10 min	-	-	38 %
13			10 min	10 min	-	39 %
14			10 min	-	10 min	41 %
15 []]			-	-	-	12 % ^[e]

[a] 20 mg of the complex was suspended in 0.5 mL of solvent, a solution with a concentration of 4.1 mM of aldehyde (mixture 1) in the specified solvent and another one of 2 mM of aminotriazole (mixture 2) in ethanol were prepared. [b] Sonicating only the suspension of the complex at room temperature. [c] Heating the suspension of the complex at 90 °C under MWI. [d] 1 mL of mixture 1 was added to the complex in suspension, and it was heated at 90 °C under MWI. [e] Experiment done without complex

Table 3. Effect of the nature of the catalyst on the efficiency of the catalytic reaction.

	Solvent		Conditions ^[a]		Yield
	Complex	Aldehyde	Catalyst	Reaction ^[b]	
1	96 % EtOH	EtOH	Nanoparticles of complex 1	10 min	76 % ^[c]
2				10 min	81 %
3				10 min	100 % ^[d]
4	96 % EtOH	EtOH	Complex 1 b	10 min	20 %
5				10 min	22 % ^[d]
6	96 % EtOH	EtOH	Complex 3	2 min	69 %
7				5 min	80 %
8				7 min	100 %
9	96 % EtOH	EtOH	Complex 2	5 min	100 %
10				10 min	100 %
11				EtOH	10 min
12	Toluene	Toluene		10 min	74 %



[a] 20 mg of the complex was suspended in 0.5 mL of solvent, a solution with a concentration of 4.1 mM of aldehyde (mixture 1) in the specified solvent and another one of 2 mM of aminotriazole (mixture 2) in ethanol were prepared, then only the suspension of the complex was sonicated for 10 min at room temperature. [b] The reaction was carried out at 90 °C under MWI. [c] Without sonication [d] Before the reaction, these samples were pre-treated by heating the mixture of the suspension of the complex and the aldehyde at 90 °C for 10 min under MWI

This is confirmed by the results obtained when 50 nm nanoparticles of the same complex **1** are used where higher yields are obtained (Table 3, entries 1–3); to obtain these nanoparticles, it is necessary to use a different methodology than the one used for the bulk complex.^[11] We then studied the effect of the counterion on the catalytic efficiency of the complex. To this end, we studied the catalytic activity of iron aminotriazole complex **1b** with sulfate as the counterion ($[\text{Fe}(\text{NH}_2\text{trz})_3]\text{SO}_4$). When the latter is used, significantly lower yields are observed than when nitrate complex **1** is used (comparison of Table 2, entries 2 and 4, and Table 3, entries 4 and 5). Even with pre-treatment of complex **1b**, the yield does not increase, which is explained by the lack of formation of the imine complex (see page 13 of the ESI). Finally, we tested the catalytic activity of iron III imine complex **3** (Table 3, entries 6–8). When the reaction is catalyzed by complex **3**, quantitative yields are obtained within 7 minutes. If we consider that iron III complexes are better Lewis acids than iron II complexes are,^[22] we would expect the former complexes to be much more efficient catalysts than the latter. The experimental results indicate that the iron III complex has a similar efficiency to that of the iron II complex (Table 3, entries 9–10). The first hypothesis that can explain this result is that, under the experimental conditions of catalysis, the iron II complex is oxidized very rapidly to iron III, and then, during or at the end of the reaction, it is reduced back to iron II. We wished to confirm or refute this hypothesis, and as discussed in the ESI (pages 30–34), while the oxidation of a small part of the complex cannot be excluded, the majority of the iron complex remains iron II. Thus, we can infer that the catalytic activities of the complex in both oxidation states are of the same order of magnitude.

A kinetic study of the reaction catalyzed by complex **1** was then carried out. Each point in Figure 5 corresponds to an

experiment. For this kinetic study, a suspension of complex **1** in ethanol was placed in an ultrasonic bath for 10 min prior to catalysis (red curve in Figure 5a). This result suggests that the catalytic mechanism of the iron II complex may not be of the Lewis acid type, as it is usually observed that iron III complexes have greater catalytic activity than iron II complexes.

The catalytic reaction is quantitative in 50 minutes. The transformation of the NH_2 functionality of aminotriazole **a** appears to be linear over time, with a change in rate after 20 minutes (yield approximately 67%). Regardless of the reaction time, the yields are much greater than those obtained when the reaction is carried out in the absence of the complex (blue curve, Figure 5a). This kinetic study confirmed that complex **1** does indeed catalyze the reaction. Furthermore, these experiments show once again that when the complex is pre-treated, the reaction is quantitative within 10 minutes (black curve, Figure 5a). If the reaction is left for 20 min, the yield remains quantitative, showing that under these experimental conditions, imine **c** is not hydrolyzed. At the end of these experiments, most of the complexes were recovered and analyzed via various techniques (IR spectroscopy, powder X-ray diffraction, scanning electron microscopy, and temperature-dependent reflectivity measurements).

Figure 5b shows the imine percentages of the complexes recovered after different catalytic times. These percentages were determined by digestion of the complex in an aqueous basic medium and proton NMR analysis of the aqueous and organic phases (see ESI). Although during pre-treatment all of the amine complex **1** was transformed into imine complex **2**, after 5 minutes of reaction, the imine functions represented approximately twelve percent of the functions present on the recovered complex (Figure 5b, black curve). Moreover, the results obtained after pre-treatment and a reaction time of 20 min show that imine complex **2** can be synthesized under these experimental conditions once aminotriazole **a** is no longer present in the medium. When complex **1** is used as a catalyst without pre-treatment, traces of imine functions are observed on the complex after 10 minutes of reaction. At 50 min, the amount of imine on the complex was estimated to be 6% (Figure 5b, red curve). The entire study of complexes recovered after catalysis is included in the ESI. One of the highlights of this study is the difference in morphology between the starting amine complex **1** and that recovered after pre-treatment and 10 minutes of catalysis. SEM images show that bulk complex **1** consists of large spherical aggregates of approximately 10 microns in size; each of these aggregates is built from a compact stack of platelets, and distinct layers of this platelet stacking are observed (Figure 6). SEM images revealed that for the amine complex recovered after pre-treatment and 10 min of catalytic reaction, large spherical aggregates disappeared, but the platelet stacks remained. Thus, performing a PSM reaction with an aldehyde followed by a PSM reaction with aminotriazole on amine complex **1** enables the particle morphology of the amine complex to be modified without causing it to lose its SCO properties. This result is of interest not only for heterogeneous catalysis, where particle size and shape affect the catalytic activity of the complex but also for all applications requiring

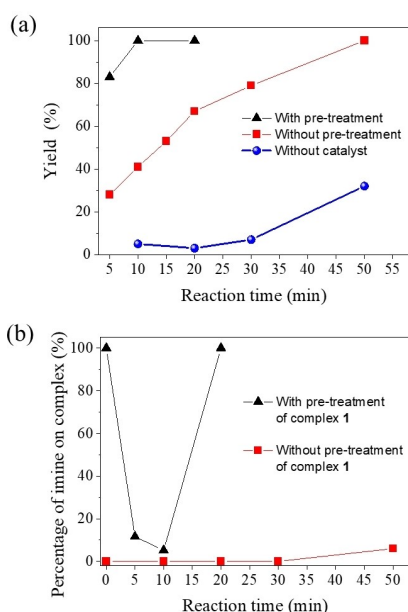


Figure 5. Kinetic study of the catalysis reaction. a) Yield of imine **c** as a function of reaction time; b) percentage of imine functionality on the complex recovered after catalysis as a function of reaction time.

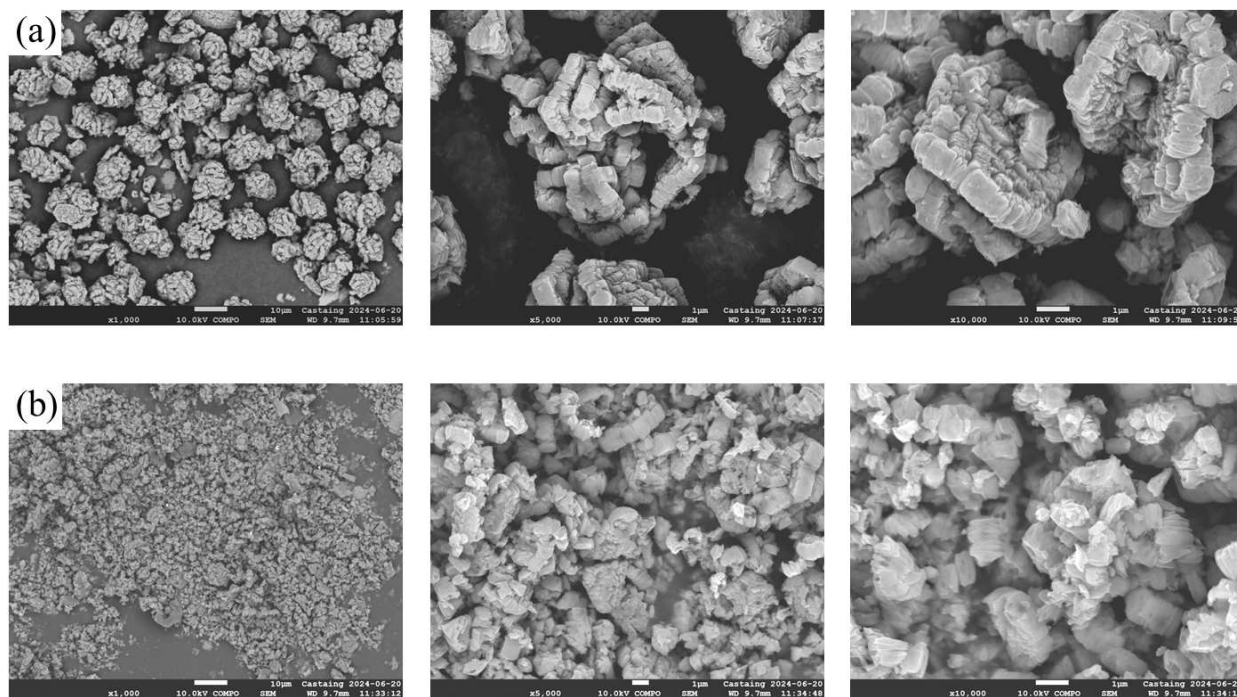


Figure 6. Scanning electron microscopy images of the a) pristine bulk complex 1 and b) the recovered complex after catalysis (with pre-treatment and 10 min of reaction).

deposition of the compound in a device. Notably, the kinetic study and particle observation were reproduced a second time using the same amine complex 1, as well as another batch of complex 1. Similar results were obtained, and this study is included in the ESI.

We then turned our attention to the mechanism of the PSM reaction, which transforms imine complex 2 into amine complex 1. We envisaged that this transformation could originate from two different types of mechanisms (Figure 7).

In the case of trans-amination, amine complex 1 is formed by nucleophilic attack of the NH_2 group of aminotriazole **a** on the imine functionality of complex 2, whereas by ligand exchange, amine complex 1 is formed by decoordination of imine **c** and coordination of aminotriazole **a** on iron. We can differentiate between these two types of mechanisms by performing a PSM reaction using a fully ^{15}N -enriched aminotriazole **a*** (Figure 8).

The presence of ^{15}N in the complex recovered after the reaction would support the ligand-exchange mechanism. On the other hand, if imine **c*** (with ^{15}N) is present in large quantities in solution, then the mechanism would be trans-amination (Figure 7). Solid-state ^{15}N NMR analysis (see ESI) of the recovered complex revealed a peak at 67.8 ppm in the ^{15}N Hahn echo MAS NMR spectra; this peak was attributed to the presence of ^{15}N in the complex, which increased the signal intensity up to 270 times,^[23] and given its low natural abundance (0.37%) and its low sensitivity, it would be nearly impossible to observe it otherwise.^[24] NMR analysis of the solution indicated that the PSM reaction was not complete, as some aminotriazole **a*** remained in the solution (Figure 9).

On the other hand, the imine formed corresponds to the ^{15}N unenriched imine **c**. If the imine **c*** is formed predominantly, then the CH signals of the triazole and imine should be multiplets due to the coupling between the protons and ^{15}N (Figure 9).^[25] Furthermore, 2D $^1\text{H}/^{15}\text{N}$ NMR analyses (HMQC and HMBC) revealed little or no correlation between protons and nitrogen for the imine formed, whereas they were clearly visible for aminotriazole **a*** (see the ESI). It would appear that amine complex 1 is formed by a PSM reaction via ligand exchange.

Finally, we explored the potential mechanism underlying this catalytic reaction. Based on the existing literature, it is plausible that the iron complex may act as a Lewis acid.^[22,26] As the interaction with the aldehyde may enhance the electrophilicity of the carbonyl group, facilitating a nucleophilic attack by the NH_2 group of aminotriazole **a**, it follows that stronger Lewis acids could promote the reaction more efficiently if this mechanism holds true. Since iron III complexes are generally stronger Lewis acids than iron II complexes, we would expect the iron III complex to exhibit greater activity. However, the observed lack of this trend suggests that the mechanism may not be based on Lewis acid activity. Furthermore, while established catalytic mechanisms exist in the literature, it's crucial to evaluate the specific reaction in question, as the mechanism can be highly dependent on both the catalyst and the substrates involved. In this case, aminotriazole **a** serves as both a catalytic substrate and a strong ligand for iron,^[27] and the NH_2 group on the complex can also react with the aldehyde. For all these reasons, the catalytic mechanism described in Figure 10 was considered.

This relatively simple mechanism consists of two PSM reactions. To generate the imine complex 2, the amine complex

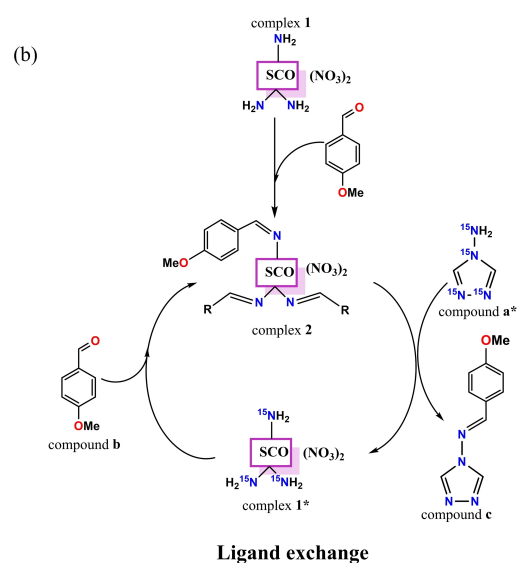
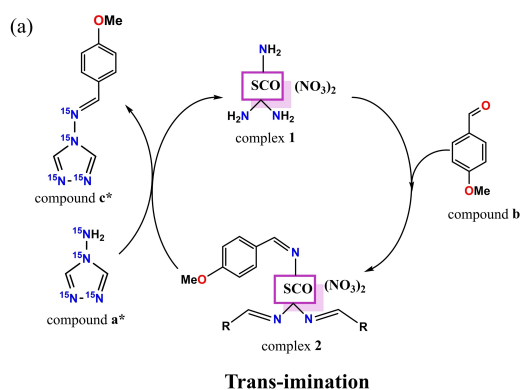


Figure 7. Proposed mechanisms for the formation of complex 1 from the complex 2.

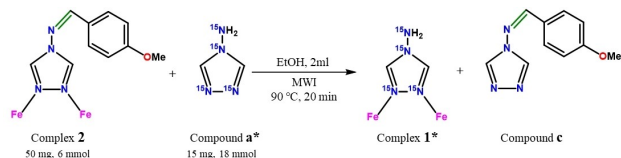


Figure 8. PSM reaction on complex 2 with aminotriazole a*.

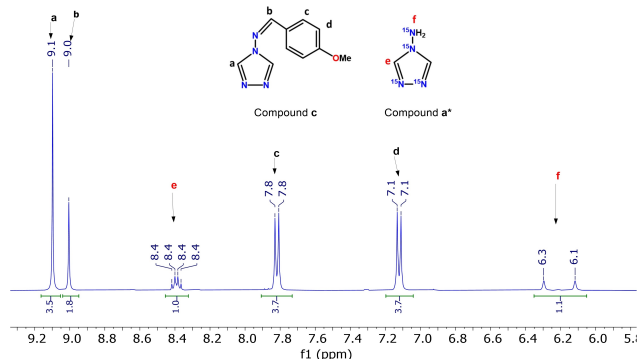


Figure 9. ^1H NMR spectrum of the solution after PSM reaction on complex 2 with aminotriazole a*.

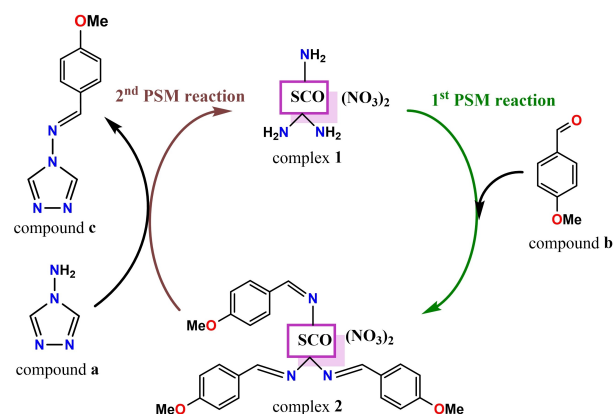


Figure 10. Proposed mechanisms where 2 consecutive PSM reactions occur, during the catalytic cycle.

1 must first undergo a PSM reaction with the aldehyde **b**. The amine complex 1 is restored by the second PSM reaction on the imine complex 2 with aminotriazole **a**. If so, and since the amount of the complex represents only 2% of the aminotriazole **a**, a significant number of PSM cycles must take place in order to obtain the imine **c** quantitatively. This implies that the NH_2 functionality of the amine complex 1 must be highly reactive towards aldehyde **b**, and that aminotriazole **a** must also be highly reactive towards the imine functionality of the complex 2. We investigated the synthesis of imine **e** catalyzed by compound 2 in order to confirm these two requirements (Figure 11).

The process requiring two PSM reactions implies that complex 2 must rapidly disappear from the medium in order for the production of imine **e** to start. This is only possible when the complex contains NH_2 functionalities. For this reason, in order to ascertain the percentage of NH_2 function and imine on the complex, we wished to analyze the complexes recovered after varying reaction periods. Additionally, the selected reaction model enables us to distinguish between the imine functionalities that were present on the original complex 2 and those that were created when an NH_2 functionality of the complex reacted with the aldehyde **d**.

Prior to delving into the findings, it is important to note that ESI presents the pre-study of the catalyzed creation of imine **e**. The experimental results indicate that the reaction reaches quantitative conversion within 5 minutes. In contrast, under non-catalyzed conditions for the same reaction time, less than 20% of imine **e** is obtained. The ^1H NMR spectrum of the solution shows the presence of imine **e** and traces of imine **c**, which results from the reaction between the imine complex 2 and aminotriazole **a** (see the ESI). Notably, within the first minute, the percentage of imine functionalities in the initial complex is estimated to be less than 5%. This finding underscores the high reactivity of aminotriazole **a** toward the imine functionalities present in the complex. Furthermore, the complex's NH_2 functionalities are highly reactive with aldehyde **d**, as evidenced by the existence of roughly 20% of imine functionalities as a result of their reaction. During the first to fourth minutes, the percentage of imine functional groups from the

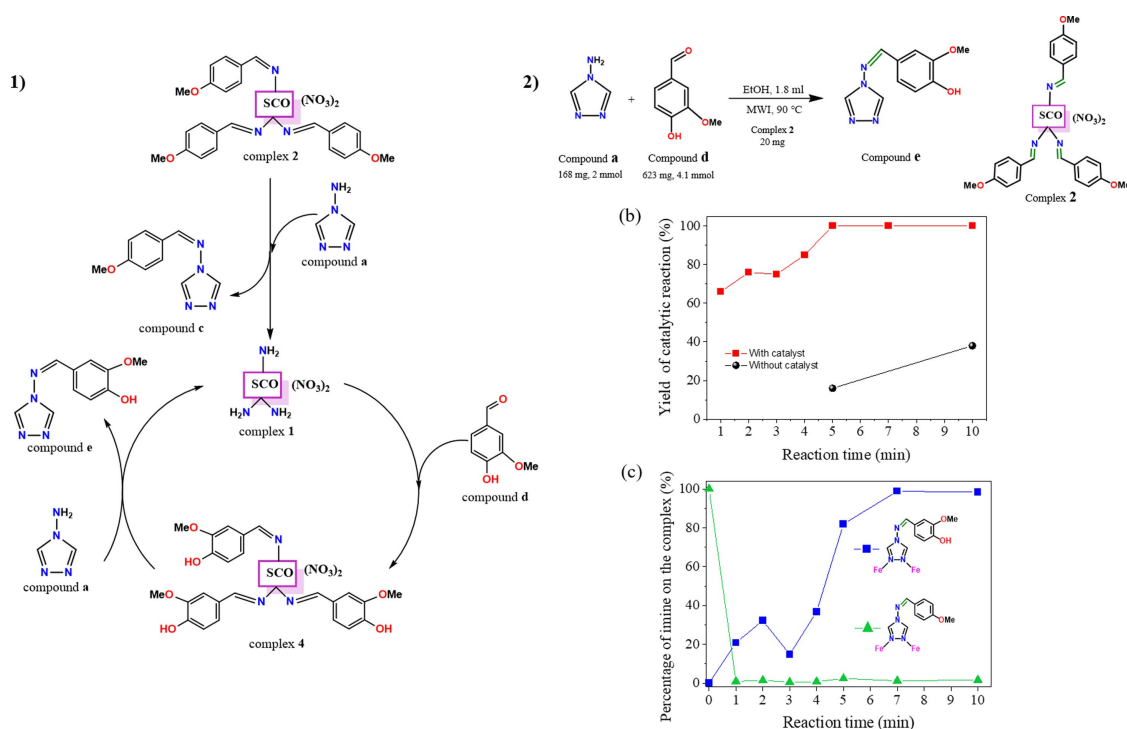


Figure 11. 1) Proposed mechanism for the formation of complex 4 from complex 2, 2) Kinetic study of the catalytic reaction between vanillin **d** and aminotriazole **a**, where the complex 2 is used as catalyst. a) Yield of the imine **e** as a function of reaction time (with and without catalyst); b) percentage of imine functionalities on the complex (from vanillin in blue, and *p*-anisaldehyde in green) as a function of reaction time.

reaction with vanillin **d** remained above 15%, eventually increasing to over 80% by the fifth minute (when few aminotriazole molecules are left in the medium). The imine complex **4** is then obtained when the catalytic reaction is longer than seven minutes (Figure 11).

Additionally, we investigated the formation of imine **c** from *p*-anisaldehyde **b**, catalyzed by the imine complex **4** (see ESI). This analysis shows that after 2 minutes of reaction, only a small fraction of the imine functionalities from the original complex **4** remain, demonstrating that the amine complex undergoes multiple catalytic cycles involving the two PSM reactions.

Lastly, we wanted to demonstrate that, in comparison to the Lewis acid type mechanism, the mechanism involving PSM reactions (Figure 12) is more prevalent. This was accomplished by examining the production of imine **e** when a stoichiometric quantity of imine complex **2** was present. A considerable amount of imine **e** should be formed by an acidic Lewis-type mechanism. The quantitative production of imine **e** should occur much faster when complex **2** is present in stoichiometric amounts than when the complex is present in catalytic quantities. In accordance with a mechanism including PSM reactions, imine **c** should be the first and quantitatively generated product (Figure 11-1). The latter results from aminotriazole's attack on the imine complex **2**. Finding the amounts of each kind of imine (**e** and **c**) enables us to identify the main catalytic mechanism. A greater amount of imine **e** would support the Lewis acid type mechanism, whereas a greater amount of imine **c** would support the PSM reaction-based mechanism.

The experimental results indicated that in 5 min of reaction, 90% of the aminotriazole **a** is converted. Notably, the reaction is initially very rapid, since in 2 minutes, only about 20% of the amine **a** remains. Whatever the reaction time, imine **c** is the product that is predominantly formed. For example, for a reaction time of 2 minutes, the quantity of imine **c** is more than 4 times greater than that of imine **e**. The complexes recovered after the competitive reaction show that less than 20% of the imine functionalities present in the complex, remain from the starting complex **2**. As already observed, aminotriazole **a** reacted very rapidly with complex **2**, but between the second and fifth minutes, the percentage of imine remained nearly the same. Furthermore, the recovered complex has imine functionalities resulting from the attack of the NH₂ groups of the complex on vanillin **d**. Thus, the formation of imine **e** can result either from the reaction of aminotriazole **a** with vanillin **d** or from the action of amine **a** on the imine functionalities present on the complex. These experiments again seem to indicate that PSM reactions on the complex may be involved in the catalytic activity of the complex. In parallel, we tested the competitive reaction using aminotriazole **a**, imine complex **4** and *p*-anisaldehyde **b** (ESI). This study confirms that aminotriazole **a** reacts preferentially with the imine complex rather than with the aldehyde present in solution.

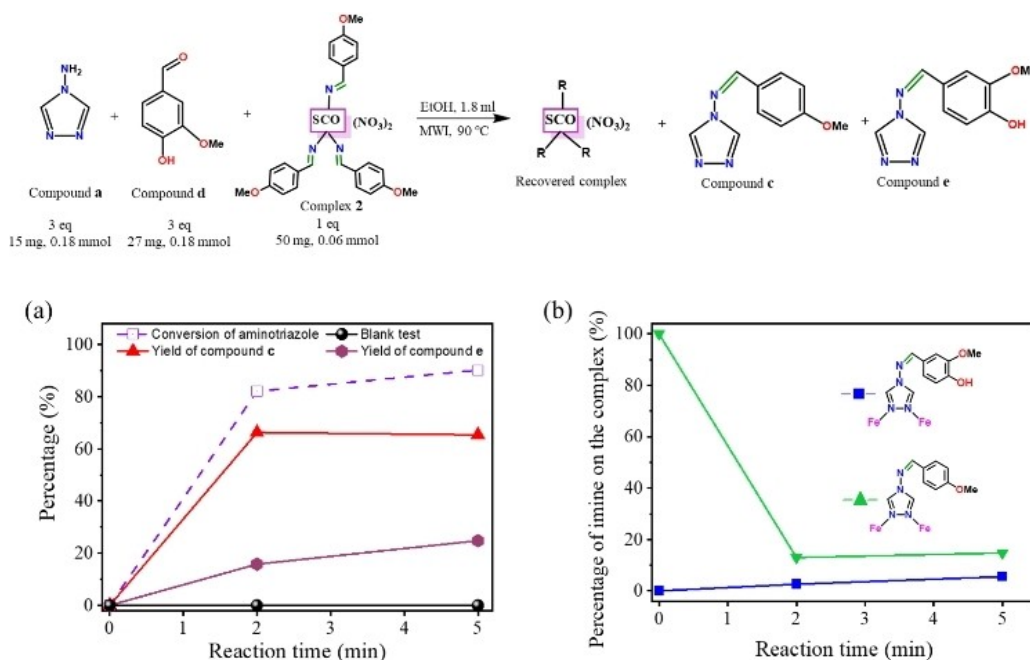


Figure 12. Kinetic study of the competitive reaction of aminotriazole **a** between vanillin **d** and complex **2**. a) Yields of imines **c** (red) and **e** (purple) as a function of reaction time; b) percentage of imine functionalities on the complex (from vanillin in blue, and *p*-anisaldehyde in green) as a function of reaction time.

Conclusions

In conclusion, the reactivity of aminotriazole **a** toward aldehydes was compared with that of the NH₂ functional groups present on the complex [Fe(NH₂trz)₃](NO₃)₂ complex. Within ten minutes, the post-synthetic reaction on the complex **1** was quantitative, whereas under the same experimental conditions, only 10% of the imine was formed from aminotriazole. On the one hand, this result indicates that a reaction starting from an insoluble reagent is not systematically slower than a reaction where all the reagents are in solution. On the other hand, this result illustrates that coordination to a metal affects the organic reactivity of the ligand. Thus, combining the PSM method with a reaction, such as the digestion of the complex, which decoordinates the ligand from iron, is also potentially interesting for the synthesis of new triazole-based organic molecules. The reaction was subsequently carried out using a mixture in which complex **1**, aminotriazole **a** and aldehyde **b** were present in stoichiometric amounts. The experimental results of this competitive reaction indicate the quantitative formation of imine in solution, and the recovered complex corresponds to amine complex **1**. The fact that the result of the competitive reaction was completely opposite to the results of the individual experiments led us to consider that the spin crossover iron complex catalyzes the formation of imine from aminotriazole **a**. This result is interesting because, to the best of our knowledge, it is the second example described in the literature of the use of this family of complexes in catalysis. Even more generally, few synthesized complexes known for their spin crossover properties have been tested in catalysis. This lack of studies is somewhat paradoxical, as there is currently a great deal of interest in the use of iron complexes in catalysis due to their catalytic activity and

accessibility, as well as the environmental sustainability of iron. An experimental study of the catalytic reaction revealed that when amine complex **1** was pre-treated with aldehyde **b**, the catalytic reaction was quantitative in less than 10 min, with an amount of iron complex equivalent to 2.3% molar with respect to aminotriazole **a**. Analysis of the iron complex recovered after the catalytic reaction yielded a wealth of information. First, as we had envisaged, the pre-treatment of the amine complex with an aldehyde led, by PSM reaction, to the formation of imine complex **2**. On the other hand, while the presence of traces of iron complex III cannot be ruled out, a very large proportion of the iron complex remains in the +II oxidation state during the catalytic reaction. Moreover, when the amine complex is used without pre-treatment, and the catalytic reaction is complete and no aminotriazole **a** remains, the recovered complex corresponds to amine complex **1**, with traces of imine functionalities on the complex. More surprisingly, when amine complex **1** is pre-treated or when imine complex **2** is used as a catalyst, from the first minute until the catalytic reaction is quantitative, the percentage of imine functionalities on the complex is well below 15%. The formation of the amine complex is explained by the reaction of aminotriazole **a** with imine complex **2**. We envisaged two different mechanisms for this PSM reaction, namely, trans-imination and/or ligand exchange on the iron center. Experiments using aminotriazole **a** with ¹⁵N suggest that the PSM reaction proceeds mainly by ligand exchange. Scanning electron microscopy analysis revealed that, while all the complexes recovered before the catalytic reaction was quantitative, the complexes had a molecular arrangement and spin crossover properties similar to those of the starting amine complex **1**, and the particles from the pre-treated amine complex or the imine complex were significantly different in size

and shape from those of the starting amine complex. On the other hand, the experimental conditions used to carry out the PSM reaction of amine complex **1** with the aldehyde also have a significant effect on the morphology of the particles of imine complex **2**. Thus, performing a PSM reaction with an aldehyde followed by a PSM reaction with aminotriazole **a** on imine complex **2** enables the particle morphology of amine complex **1** to be modified without causing it to lose its excellent SCO properties. This result is of interest not only for heterogeneous catalysis, where particle size and shape affect the catalytic activity of the complex but also for the proper integration of SCO into devices. The iron III imine complex has a catalytic activity close to that of the iron II imine complex. This result is surprising, as iron III complexes are generally better Lewis acids than their iron II analogs are, and imine formation from aldehydes is efficiently catalyzed by Lewis acids. As previously indicated, we are confident that the iron II complex remains under this oxidation state during the catalytic reaction. For these two reasons, we concluded that the mechanism of the reaction may not be of the Lewis acid type, and we envisaged that PSM reactions may be involved in the catalytic activity of this iron II complex. The two types of experiments carried out to confirm or refute this hypothesis support the involvement of PSM reactions in the catalytic mechanism. The first experiments showed that after just one minute of catalysis, very few imine functionalities remain from the initial complex, and imine functionalities, originating from the aldehyde used as a catalysis substrate, are visible on the complex. This result indicates that the amine complex can rapidly undergo many catalytic cycles consisting of the two PSM reactions. This criterion is essential for the involvement of PSM reactions in the catalytic mechanism. The second type of experiment involves a competitive reaction in which the reaction mixture contains aminotriazole **a**, an aldehyde and imine complex **2** in stoichiometric amounts. The preferential attack of aminotriazole **a** on imine complex **2** rather than on the aldehyde supports a mechanism involving PSM reactions. In the case of a Lewis acid mechanism, the presence of the complex in noncatalytic quantities would have greatly favored the attack of aminotriazole **a** on the aldehyde. This research, combined with the fact that we have also recently shown a strong influence of the spin state on the efficiency of the PSM method on this iron complex, allows us to be optimistic about the possibility of considering spin crossover complexes as new candidates for the realization of switchable catalysis. Work is currently underway in our group to demonstrate the effect of the spin state on the catalytic efficiency of 1D coordination polymers with SCO properties.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

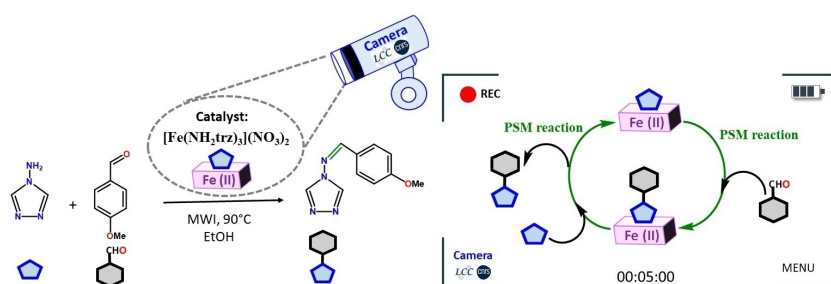
The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Spin crossover · Iron complex · Post-synthetic modification method · Catalysis · Imine formation

- [1] a) M. Kondo, H. Tatewaki, S. Masaoka, *Chemical Society Reviews* **2021**, *50*, 6790–6831; b) J. Wen, F. Wang, X. Zhang, *Chemical Society Reviews* **2021**, *50*, 3211–3237; c) G. A. Filonenko, R. van Putten, E. J. M. Hensen, E. A. Pidko, *Chemical Society Reviews* **2018**, *47*, 1459–1483; d) S. H. Kyne, G. Lefèvre, C. Ollivier, M. Petit, V.-A. Ramis Cladera, L. Fensterbank, *Chemical Society Reviews* **2020**, *49*, 8501–8542.
- [2] a) O. V. Khavryuchenko, V. D. Khavryuchenko, D. Su, *Chinese Journal of Catalysis* **2015**, *36*, 1656–1661; b) A. L. Buchachenko, V. L. Berdinsky, *Chemical Reviews* **2002**, *102*, 603–612; c) A. Cao, J. K. Nørskov, *ACS Catalysis* **2023**, *13*, 3456–3462; d) P. Pérez, J. Andrés, V. Safont, O. Tapia, R. Contreras, *The Journal of Physical Chemistry A* **2002**, *106*, 5353–5357.
- [3] G.-Z. Huang, Y.-S. Xia, F. Yang, W.-J. Long, J.-J. Liu, J.-P. Liao, M. Zhang, J. Liu, Y.-Q. Lan, *J. Am. Chem. Soc.* **2023**, *145*, 26863–26870.
- [4] A. Enríquez-Cabrera, Y. Lai, L. Salmon, L. Routaboul, A. Bousseksou, *submitted articles (still under revision with the publishers)* **2024**.
- [5] G. Molnár, S. Rat, L. Salmon, W. Nicolazzi, A. Bousseksou, *Adv. Mater.* **2018**, *30*, 1703862.
- [6] a) G.-M. Rotaru, E. Codjovi, P.-R. Dahoo, I. Maurin, J. Linares, A. Rotaru, *Symmetry* **2021**, *13*, 1148; b) M. A. Halcrow, *Spin-crossover materials: properties and applications*, John Wiley & Sons, **2013**; c) C. M. Quintero, A. Il'ya, L. Salmon, G. Molnár, C. Bergaud, A. Bousseksou, *Journal of Materials Chemistry* **2012**, *22*, 3745–3751.
- [7] a) V. Shalabaeva, K. Ridier, S. Rat, M. D. Manrique-Juarez, L. Salmon, I. Séguy, A. Rotaru, G. Molnár, A. Bousseksou, *Applied Physics Letters* **2018**, *112*, 013301; b) J. Dugay, M. Aarts, M. Giménez-Marqués, T. Kozlova, H. Zandbergen, E. Coronado, H. Van Der Zant, *Nano letters* **2017**, *17*, 186–193; c) E. Mishra, T. K. Ekanayaka, K. A. McElveen, R. Y. Lai, P. A. Dowben, *Organic Electronics* **2022**, *105*, 106516; d) C. Lefter, I. Y. A. Gural'skiy, H. Peng, G. Molnár, L. Salmon, A. Rotaru, A. Bousseksou, P. Demont, *physica status solidi (RRL)–Rapid Research Letters* **2014**, *8*, 191–193; e) A. Rotaru, A. Il'ya, G. Molnár, L. Salmon, P. Demont, A. Bousseksou, *Chemical Communications* **2012**, *48*, 4163–4165.
- [8] K. Ridier, A.-C. Bas, Y. Zhang, L. Routaboul, L. Salmon, G. Molnár, C. Bergaud, A. Bousseksou, *Nat Commun* **2020**, *11*, 3611.
- [9] a) B. Tondou, M. Piedrahita-Bello, L. Salmon, G. Molnár, A. Bousseksou, *Sensors and Actuators A: Physical* **2022**, *335*, 113359; b) J. E. Angulo-Cervera, M. Piedrahita-Bello, B. Martin, S. E. Alavi, W. Nicolazzi, L. Salmon, G. Molnár, A. Bousseksou, *Materials Advances* **2022**, *3*, 5131–5137; c) M. Piedrahita-Bello, J. E. Angulo-Cervera, A. Enriquez-Cabrera, G. Molnár, B. Tondou, L. Salmon, A. Bousseksou, *Materials Horizons* **2021**, *8*, 3055–3062; d) M. Piedrahita-Bello, X. Yang, S. E. Alavi, G. Molnár, L. Salmon, A. Bousseksou, *Sensors and Actuators B: Chemical* **2023**, *393*, 134147.
- [10] a) A. Enríquez-Cabrera, L. Routaboul, L. Salmon, A. Bousseksou, *Dalton Transactions* **2019**, *48*, 16853–16856; b) A. Enríquez-Cabrera, K. Ridier, L. Salmon, L. Routaboul, A. Bousseksou, *European Journal of Inorganic Chemistry* **2021**, *2021*, 2000–2016.
- [11] A. Enriquez-Cabrera, L. Getzner, L. Salmon, L. Routaboul, A. Bousseksou, *New J. Chem.* **2022**, *46*, 22004–22012.
- [12] I. Y. A. Gural'skiy, S. I. Shylin, V. Ksenofontov, W. Tremel, *European Journal of Inorganic Chemistry* **2017**, *2017*, 3125–3131.
- [13] a) I. Prat, A. Company, T. Corona, T. Parella, X. Ribas, M. Costas, *Inorganic Chemistry* **2013**, *52*, 9229–9244; b) A. C. McQuilken, H. Matsumura, M. Dürr, A. M. Confer, J. P. Sheckelton, M. A. Siegler, T. M. McQueen, I. Ivanović-Burmazović, P. Moëgne-Loccoz, D. P. Goldberg, *Journal of the American Chemical Society* **2016**, *138*, 3107–3117; c) D. Umeyama, A. Takai, K. Sonobe, *Inorganic Chemistry* **2022**, *61*, 1697–1703

- [14] a) P. Chen, H.-N. Chen, H.N.C. Wong, X.-S. Peng, *Organic and Biomolecular Chemistry* **2023**, *21*, 6083–6095; b) X.-F. Duan, *Chemical Communications* **2020**, *56*, 14937–14961; c) E. Balaraman, A. Nandakumar, G. Jaiswal, M. K. Sahoo, *Catalysis Science and Technology* **2017**, *7*, 3177–3195; d) D. Wang, D. Astruc, *Chemical Society Reviews* **2017**, *46*, 816–854; e) T. L. Mako, J. A. Byers, *Inorganic Chemistry Frontiers* **2016**, *3*, 766–790; f) G. Bauer, X. Hu, *Inorganic Chemistry Frontiers* **2016**, *3*, 741–765; g) R. Hudson, Y. Feng, R. S. Varma, A. Moores, *Green Chem.* **2014**, *16*, 4493–4505; h) S. Rana, J. P. Biswas, S. Paul, A. Paik, D. Maiti, *Chemical Society Reviews* **2021**, *50*, 243–472; i) I. Bauer, H.-J. Knölker, *Chemical Reviews* **2015**, *115*, 3170–3387; j) K. Junge, K. Schröder, M. Beller, *Chemical Communications* **2011**, *47*, 4849; k) F. Jia, Z. Li, *Org. Chem. Front.* **2014**, *1*, 194–214; l) M. D. Greenhalgh, A. S. Jones, S. P. Thomas, *ChemCatChem* **2014**, *7*, 190–222; m) A. Stadler, R. Gil, S. Bezzenine, J. Hannedouche, *L'Actualité Chimique* **2022**, *473–474*, 33–39.
- [15] a) R. Tokala, S. Bale, I. P. Janrao, A. Vennela, N. P. Kumar, K. R. Senwar, C. Godugu, N. Shankaraiah, *Bioorganic and Medicinal Chemistry Letters* **2018**, *28*, 1919–1924; b) Q. Zhang, X. Liu, W. Gan, J. Wu, H. Zhou, Z. Yang, Y. Zhang, M. Liao, P. Yuan, S. Xu, P. Zheng, W. Zhu, *ACS Omega* **2020**, *5*, 16482–16490; c) N. Chandna, J. K. Kapoor, J. Grover, K. Bairwa, V. Goyal, S. M. Jachak, *New Journal of Chemistry* **2014**, *38*, 3662; d) N. Thamban Chandrika, S. K. Shrestha, H. X. Ngo, O. V. Tsodikov, K. C. Howard, S. Garneau-Tsodikova, *Journal of Medicinal Chemistry* **2017**, *61*, 158–173; e) E. L. Luzina, A. V. Popov, *European Journal of Medicinal Chemistry* **2010**, *45*, 5507–5512.
- [16] a) A. B. Lysenko, G. A. Senchyk, K. V. Domasevitch, J. R. Hauser, D. Fuhrmann, M. Kobalz, H. Krautscheid, P. Neves, A. A. Valente, I. S. Goncalves, *Inorganic Chemistry* **2015**, *54*, 8327–8338; b) W. J. Wang, Z. H. Sun, S. C. Chen, J. F. Qian, M. Y. He, Q. Chen, *Applied Organometallic Chemistry* **2021**, *35*; c) A. Günther, Y. Deja, M. Kilic, K. Tran, P. Kotra, F. Renz, W. Kowalsky, B. Roth, *Scientific Reports* **2024**, *14*; d) S. Dutta, S. Mukherjee, O. T. Qazvini, A. K. Gupta, S. Sharma, D. Mahato, R. Babarao, S. K. Ghosh, *Angewandte Chemie International Edition* **2021**, *61*; e) A. Mohanty, S. Kumar, S. K. Tiwari, *Materials Today Communications* **2021**, *27*, 102439; f) H. Gao, J. N. M. Shreeve, *RSC Advances* **2014**, *4*, 24874; g) G. Drake, T. Hawkins, A. Brand, L. Hall, M. McKay, A. Vij, I. Ismail, *Propellants, Explosives, Pyrotechnics* **2003**, *28*, 174–180; h) S. Wang, Z. Li, Y. Zhang, X. Liu, J. Han, X. Li, Z. Liu, S. Liu, W. C. H. Choy, *Advanced Functional Materials* **2019**, *29*, 1900417.
- [17] H. Eshghi, M. Bakavoli, J. Abedini-Torghabeh, M. Rahimizadeh, *Chin. Chem. Lett.* **2012**, *23*, 1153–1156.
- [18] a) G. Arora, T. Sahni, S. Sharma, D. Verma, *International Research Journal of Pure and Applied Chemistry* **2020**, *21*, 44–56; b) K. M. Khan, S. Siddiqui, M. Saleem, M. Taha, S. M. Saad, S. Perveen, M. I. Choudhary, *Bioorganic and Medicinal Chemistry* **2014**, *22*, 6509–6514; c) F. D. Popp, *European journal of medicinal chemistry* **1989**, *24*, 313–315.
- [19] a) R. Herchel, L. Pavelek, Z. Trávníček, *Dalton Transactions* **2011**, *40*, 11896; b) J. Gou, Y.-S. Hu, J. Xu, N. Bi, H.-L. Gao, J.-Z. Cui, L. Jia, *Polyhedron* **2023**, *242*, 116484; c) A.-M. Li, E. Rentschler, *Polyhedron* **2018**, *154*, 364–372; d) S.-H. Zhang, J.-M. Wang, H.-Y. Zhang, Y.-P. Fan, Y. Xiao, *Dalton Transactions* **2017**, *46*, 410–419; e) A. M. Li, T. Hochdörffer, J. A. Wolny, V. Schünemann, E. Rentschler, *European Journal of Inorganic Chemistry* **2018**, *2018*, 4190–4199; f) B. Zhai, Z. Y. Li, X. F. Zhang, X. X. Wu, J. H. Guo, J. Z. Huo, B. Ding, *Zeitschrift für anorganische und allgemeine Chemie* **2016**, *642*, 260–267; g) D.-B. Dang, M.-M. Li, Y. Bai, R.-Q. Ning, *Synthetic Metals* **2012**, *162*, 2075–2080.
- [20] a) B. S. Creaven, M. Devereux, A. Foityn, S. McClean, G. Rosair, V. R. Thangella, M. Walsh, *Polyhedron* **2010**, *29*, 813–822; b) E. S. Bazhina, A. A. Bovkunova, M. A. Shmelev, A. A. Korlyukov, A. A. Pavlov, L. Hochvaldová, L. Kvítek, A. Panáček, P. Kopel, I. L. Eremenko, M. A. Kiskin, *Inorganica Chimica Acta* **2023**, *547*, 121359; c) S.-M. Zhang, H.-Y. Zhang, Q.-P. Qin, J.-W. Fei, S.-H. Zhang, *J. Inorg. Biochem.* **2019**, *193*, 52–59.
- [21] a) A. Manna, E. Sundaram, C. Amutha, V. S. Vasantha, *ACS Omega* **2018**, *3*, 6243–6250; b) J. Albarrán-Velo, M. López-Iglesias, V. Gotor, V. Gotor-Fernández, I. Lavandera, *RSC Adv.* **2017**, *7*, 50459–50471; c) H. Nabipour, H. Niu, X. Wang, S. Batool, Y. Hu, *Reactive and Functional Polymers* **2021**, *168*, 105034; d) H. Nabipour, S. Rohani, Y. Hu, *Journal of Environmental Chemical Engineering* **2024**, *12*, 112121.
- [22] J. I. Padrón, V. S. Martín, *Catalysis by Means of Fe-Based Lewis Acids. In: Iron Catalysis. Topics in Organometallic Chemistry*, vol 33, Springer, Berlin, Heidelberg, **2011**.
- [23] F. Henot, B. Vibert, J. Boissbouvier, *L'Actualité chimique* **2024**, *491*, 63–64.
- [24] D. Gajan, G. Lapadula, M. Schwarzwälder, C. Copéret, *L'Actualité chimique* **2012**, *2013*, 82–89.
- [25] a) R. M. Claramunt, D. Sanz, S. H. Alarcón, M. Pérez Torralba, J. Elguero, C. Foces-Foces, M. Pietrzak, U. Langer, H.-H. Limbach, *Angewandte Chemie International Edition* **2001**, *40*, 420–423; b) D. Sanz, M. Pérez-Torralba, S. H. Alarcón, R. M. Claramunt, C. Foces-Foces, J. Elguero, *The Journal of Organic Chemistry* **2002**, *67*, 1462–1471.
- [26] a) A. F. Zahoor, R. Iftikhar, S. Ahmad, A. U. Haq, S. Naheed, *Current Organic Synthesis* **2022**, *19*, 569–577; b) P. Ghosh, B. Saha, G. C. Pariyar, A. Tamang, R. Subba, *Tetrahedron Letters* **2016**, *57*, 3618–3621; c) J. Safaei-Ghomi, A. Ziarati, *Journal of the Iranian Chemical Society* **2012**, *10*, 135–139; d) W. Xu, T. Ollevier, F. Kleitz, *ACS Catalysis* **2018**, *8*, 1932–1944; e) F. Viton, G. Bernardinelli, E. P. Kündig, *Journal of the American Chemical Society* **2002**, *124*, 4968–4969; f) A. R. Oveisi, K. Zhang, A. Khorramabadi-zad, O. K. Farha, J. T. Hupp, *Scientific Reports* **2015**, *5*; g) G. K. Surya Prakash, I. Bychinskaya, E. R. Martinez, T. Mathew, G. A. Olah, *Catalysis Letters* **2013**, *143*, 303–312; h) J. R. Ludwig, P. S. Phan, C. C. McAtee, P. M. Zimmerman, J. J. Devery, C. S. Schindler, *Journal of the American Chemical Society* **2017**, *139*, 10832–10842; i) C. S. Hanson, M. C. Psaltakis, J. J. Cortes, J. J. Devery, *Journal of the American Chemical Society* **2019**, *141*, 11870–11880; j) A. Dhakshinamoorthy, M. Alvaro, P. Horcajada, E. Gibson, M. Vishnuvarthan, A. Vimont, J.-M. Grenèche, C. Serre, M. Daturi, H. Garcia, *ACS Catalysis* **2012**, *2*, 2060–2065; k) H. Veisi, B. Maleki, F. H. Eshbala, H. Veisi, R. Masti, S. S. Ashrafi, M. Baghayeri, *RSC Advances* **2014**, *4*, 30683; l) A. Dhakshinamoorthy, M. Alvaro, H. Chevreau, P. Horcajada, T. Devic, C. Serre, H. Garcia, *Catal. Sci. Technol.* **2012**, *2*, 324–330; m) S. B. Abd Hamid, S. J. Teh, Y. S. Lim, *BioResources* **2015**, *10*, 5974–5986; n) H. Albright, H. L. Vonesh, C. S. Schindler, *Organic Letters* **2020**, *22*, 3155–3160; o) H. Albright, P. S. Riehl, C. C. McAtee, J. P. Reid, J. R. Ludwig, L. A. Karp, P. M. Zimmerman, M. S. Sigman, C. S. Schindler, *Journal of the American Chemical Society* **2018**, *141*, 1690–1700; p) J. Jankowska, J. Paradowska, J. Mlynarski, *Tetrahedron Letters* **2006**, *47*, 5281–5284; q) J. S. Yadav, B. V. S. Reddy, U. V. S. Reddy, K. Praneeth, *Tetrahedron Letters* **2008**, *49*, 4742–4745; r) M. F. Mayer, Q. Wang, M. M. Hossain, *Journal of Organometallic Chemistry* **2001**, *630*, 78–83.
- [27] a) O. Roubeau, P. Gamez, S. J. Teat, *European Journal of Inorganic Chemistry* **2013**, *2013*, 934–942; b) D. Wang, R. Zhang, J. Liu, B. Ji, W. Wang, M. Peng, C. Huang, L. Cheng, Y. Ding, *Polymers* **2023**, *15*, 2363; c) M. S. Kilic, J. Brehme, J. Pawlak, K. Tran, F. W. Bauer, T. Shiga, T. Suzuki, M. Nihei, R. F. Sindelar, F. Renz, *Polymers* **2023**, *15*, 2365; d) O. Shakirova, M. Grunert, D. Y. Naumov, F. Gütllich, L. Lavrenova, *Journal of Structural Chemistry* **2010**, *51*, 45–52; e) M. Seredyuk, A. B. Gaspar, V. Ksenofontov, S. Reiman, Y. Galyametdinov, W. Haese, E. Rentschler, P. Gütllich, *Chemistry of materials* **2006**, *18*, 2513–2519; f) T. Fujigaya, D. L. Jiang, T. Aida, *Chemistry—An Asian Journal* **2007**, *2*, 106–113; g) T. Fujigaya, D.-L. Jiang, T. Aida, *Journal of the American Chemical Society* **2005**, *127*, 5484–5489; h) E. Rentschler, C. V. Malotki, *Inorganica Chimica Acta* **2008**, *361*, 3646–3653; i) M. M. Dirtu, A. Rotaru, D. Gillard, J. Linares, E. Codjovi, B. Tinant, Y. Garcia, *Inorganic chemistry* **2009**, *48*, 7838–7852; j) M. M. Dirtu, Y. Garcia, M. Nica, A. Rotaru, J. Linares, F. Varret, *Polyhedron* **2007**, *26*, 2259–2263; k) M. B. Bushuev, D. P. Pishchur, I. V. Korolkov, K. A. Vinogradova, *Physical Chemistry Chemical Physics* **2017**, *19*, 4056–4068; l) I. Bräunlich, A. Sánchez-Ferrer, M. Bauer, R. Schepper, P. Knüsel, J. Dshemuchadse, R. Mezzenga, W. Caseri, *Inorganic chemistry* **2014**, *53*, 3546–3557.
- [28] C. Allen, A. Bell, *Org. Synth* **1944**, *24*, 12.

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The spin crossover iron complex, with the formula $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$, catalyzes imine formation from 4-amino-1,2,4-triazole and aldehyde. During catalysis, the iron complex undergoes two different PSM

reactions: the first with an aldehyde and the second with an aminotriazole. These PSM reactions are thought to be involved in the catalytic mechanism of this iron-based coordination polymer.

Y. Lai, A. Enríquez-Cabrera, A. Ronci, L. Salmon, L. Routaboul*, A. Bousseksou*

1 – 13

When the Study of the Post-Synthetic Modification Method on a 1D Spin Crossover Coordination Polymer Highlights its Catalytic Activity

