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Lucile Chatelain, Federica Arrigoni, Philippe Schollhammer, Giuseppe Zampella. C–Cl Bond Activation at Rotated vs Unrotated Dinuclear Site Related to [FeFe]-Hydrogenases. *Inorganic Chemistry*, 2023, 62 (51), pp.20913-20918. 10.1021/acs.inorgchem.3c03481 . hal-04373323

**HAL Id: hal-04373323**

**<https://hal.science/hal-04373323v1>**

Submitted on 6 Jun 2024

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# C-Cl bond activation at rotated vs unrotated dinuclear site related to [FeFe]-hydrogenases

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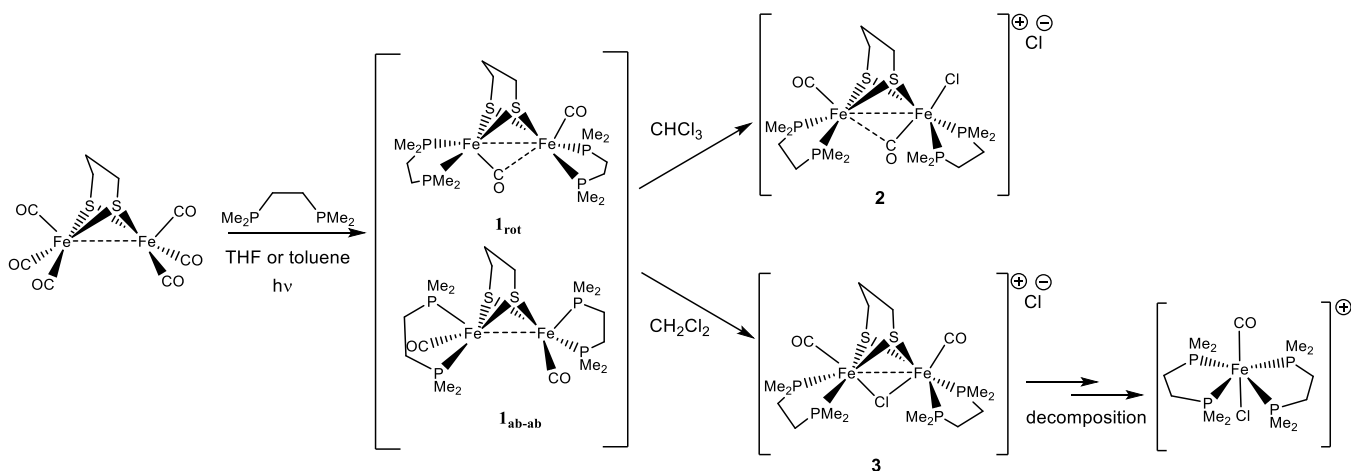
## ABSTRACT

The novel dinuclear complex related to the [FeFe]-hydrogenases active site,  $[\text{Fe}_2(\mu\text{-pdt})(\kappa^2\text{-dmpe})_2(\text{CO})_2]$  (**1**), is highly reactive towards chlorinated compounds  $\text{CH}_x\text{Cl}_{4-x}$  ( $x = 1, 2$ ) affording selectively terminal or bridging chloro di-iron isomers through a C-Cl bond activation. DFT calculations suggest a cooperative mechanism involving a formal concerted regioselective chloronium transfer depending on the unrotated or rotated conformation of two isomers of **1**.

The activation of C-Cl bonds by transition metal complexes represents a crucial objective motivated by economic and environmental imperatives, whether for employing chlorocarbons as substrates or facilitating dechlorination processes.<sup>1-10</sup> While numerous mononuclear complexes able to activate small  $\text{CH}_x\text{Cl}_{4-x}$  ( $x = 1, 2$ ) substrates have been reported,<sup>11-15</sup> well-defined polymetallic complexes (generally based on 2<sup>nd</sup>-3<sup>rd</sup> row transition metals), which induce

the cleavage of C-Cl bonds of polychlorinated molecules, are more scarce.<sup>16–30</sup> Despite the existence of numerous di-iron complexes inspired by the [FeFe]-hydrogenases metal cofactor, their “promiscuous” activity, i.e., other than that concerning the H<sup>+</sup>/H<sub>2</sub> conversion,<sup>31–40</sup> has been little explored.<sup>41–46</sup> The activation of chlorinated organic molecules with such Fe<sub>2</sub> complexes has never been reported. Here we present the reactivity towards polychlorinated molecules of the bis-chelated complex [Fe<sub>2</sub>(μ-pdt)(κ<sup>2</sup>-dmpe)<sub>2</sub>(CO)<sub>2</sub>] (**1**) (dmpe: 1,2-bis(dimethylphosphino)ethane; pdt: propanedithiolate), a new example of tetrasubstituted diiron dithiolate complex.<sup>47–55</sup> The cleavage of C-Cl bonds through an unusual cooperative bimetallic mechanism, involving a formal regioselective chloronium transfer, has been investigated by DFT.

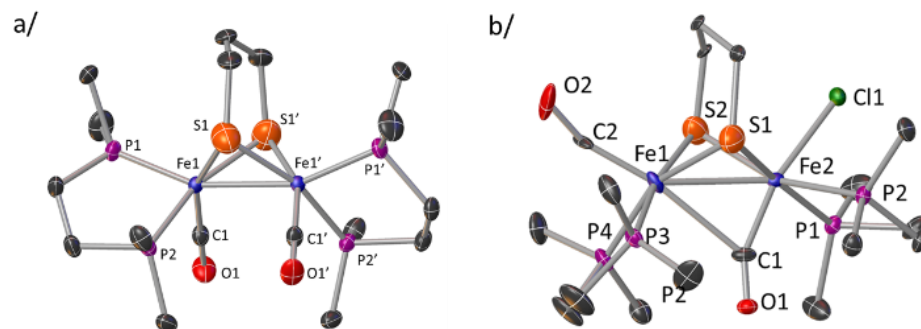
**1** was prepared as a dark brown powder, in good yields, by UV irradiation (365 nm) of THF or toluene solutions of the hexacarbonyl precursor [Fe<sub>2</sub>(μ-pdt)(CO)<sub>6</sub>], in the presence of an excess of dmpe (3-4 equiv.) (Scheme 1).



**Scheme 1.** Syntheses of complexes **1-3**

Single crystals of **1**, suitable for an X-ray analysis, grew in saturated hexane solution at room temperature. The solid-state structure revealed that the two dmpe ligands adopt an apical-basal disposition (Fig. 1a). The structure of **1** is typical of [Fe<sub>2</sub>(μ-SR)<sub>2</sub>L<sub>6</sub>]

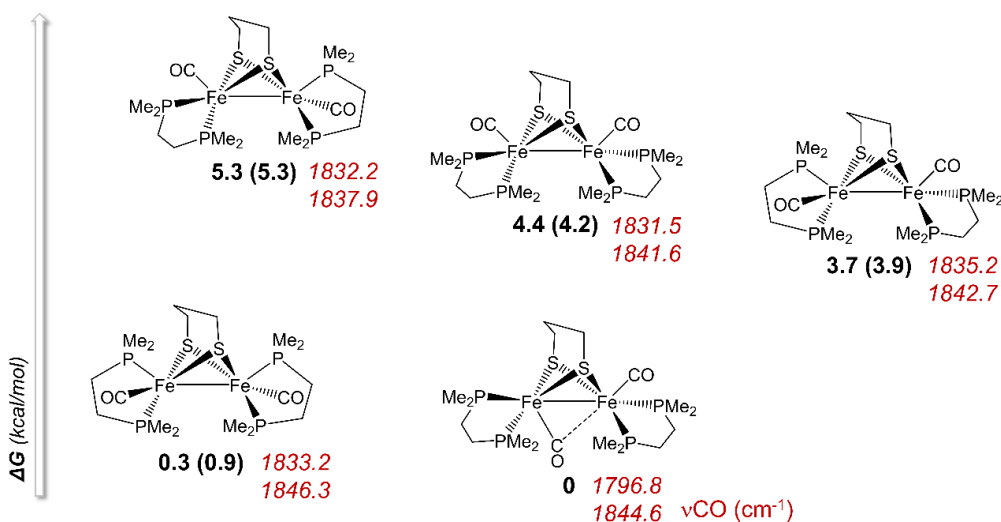
compounds with a butterfly  $\{\text{Fe}_2\text{S}_2\}$  core.<sup>48,49,51,52,56</sup> The Fe-Fe distance, of 2.5197(6) Å, is shorter than those observed in analogous complexes [2.5678(4)-2.6164(6) Å].<sup>48,49,51,52</sup>



**Figure 1** Crystallographic structures of **a/**  $[\text{Fe}_2(\mu\text{-pdt})(\kappa^2\text{-dmpe})_2(\text{CO})_2]$  (**1**). Atoms labeled with 'are obtained with a 2-fold axis ( $1-x, +y, \frac{1}{2}-z$ ); **b/**  $[\text{Fe}_2(\mu\text{-pdt})(\mu\text{-CO})(\kappa^2\text{-dmpe})_2(\text{CO})\text{Cl}]\text{Cl}\cdot 4\text{CHCl}_3$  (**2**· $4\text{CHCl}_3$ ). Displacement ellipsoids are drawn at the 40% probability level and disorders,  $\text{CHCl}_3$  solvent molecules,  $\text{Cl}^-$  counter ion and hydrogen atoms are omitted for clarity

The  $^1\text{H}$  NMR spectrum of a freshly prepared solution of **1** in  $\text{CD}_2\text{Cl}_2$  showed ill-resolved resonances between 2.27 and 1.42 ppm assigned to the signals of both dmpe and pdt ligands (Fig. S9). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  revealed at room temperature a broad singlet at 60.0 ppm which suggests a fluxional motion of the diphosphine. Upon cooling at 213 K in  $\text{CD}_2\text{Cl}_2$ , this signal splits into two singlets at 69.1 and 52.3 ppm (Fig. S10), which could be attributed to the isomer **1<sub>ab-ab</sub>** observed in solid state.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at 203K in  $\text{CD}_2\text{Cl}_2$  (Fig. S12) confirms the symmetry of **1**. It is noteworthy that depending on the solvent, further resonances were detected in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in addition to the broad signal of **1**, which suggests the presence in solution of an isomer of **1<sub>ab-ab</sub>**. In  $\text{C}_6\text{D}_6$  and  $\text{THF-D}_8$  solution, two additional signals at 78 and 68 ppm were

observed (Fig. S11), which excludes a bis-(dibasal) isomer. Moreover, the IR spectrum of **1** in THF displays two strong  $\nu(\text{CO})$  bands at 1863 and 1843  $\text{cm}^{-1}$  (Fig. S5) which are, as expected, shifted to lower frequencies compared to those of its dppv (cis-1,2-bis(diphenylphosphino)ethylene) analog<sup>51</sup> and very close to that of  $[\text{Fe}_2(\mu\text{-pdt})(\text{PMe}_3)_4(\text{CO})_2]$ .<sup>48</sup> Unlike these latter four-substituted compounds, a third weak band lies at 1799  $\text{cm}^{-1}$  in the range of  $\nu(\mu\text{-CO})$  bands.<sup>57–59</sup> To gain further insights into the isomeric stability, a thermodynamic speciation of **1** was carried out by DFT in both  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  solvents (Fig. 2 and ESI-section VI).<sup>60–62</sup> Two isoenergetic structures were found as the most stable: a bis-(apical-basal) unrotated isomer **1<sub>ab-ab</sub>**, that resembles the X-ray structure of **1**, and unexpectedly, a bis-(dibasal) rotated form (**1<sub>rot</sub>**). The DFT IR  $\nu(\text{CO})$ s suggest that the three bands experimentally observed (1795, 1836 and 1856  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) likely arise from an equilibrium mixture of these two low-energy isomers in solution. Specifically, the band at 1795  $\text{cm}^{-1}$  can be assigned to the semi-bridging CO in **1<sub>rot</sub>**. No other rotated isomer was found as stable structure. Moreover, calculated  $^{31}\text{P}$  NMR chemical shifts of **1<sub>ab-ab</sub>** and **1<sub>rot</sub>** agree with experimental observations (Fig. S25).



**Figure 2.** Thermodynamic speciation of **1**. Relative free energies (kcal/mol) in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> (in parenthesis) and  $\nu(\text{CO})$ s (cm<sup>-1</sup>, gas phase, red values) are reported.

The dissolution of **1** into CHCl<sub>3</sub> (experiments performed both in light and in dark to prevent the formation of halocarbon radicals) afforded serendipitously X-ray quality crystals of [Fe<sub>2</sub>( $\mu$ -pdt)( $\mu$ -CO)( $\kappa^2$ -dmpe)<sub>2</sub>(CO)Cl]Cl $\cdot$ 4CHCl<sub>3</sub> **2**·4(CHCl<sub>3</sub>) (Fig. 1b). **2** could be readily and quantitatively prepared, at room temperature, by addition of a drop of CHCl<sub>3</sub> to a solution of **1** in hexane, that induced its instant precipitation in excellent yield (96%). Analysis of the volatiles by NMR spectroscopy revealed the presence of a mixture of dechlorinated molecules CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub> (ESI-Section VII). The X-ray structure of **2** reveals a cationic {Fe<sub>2</sub>S<sub>2</sub>} core with two dmpe ligands in dibasal position and a bridging CO. A second carbonyl group and a Cl ligand in terminal apical positions complete the Fe coordination sphere. The Fe-Fe distance (2.629(2) Å) is much longer than that of other di-ferrous complexes bearing a bridging CO [2.5135(12)-2.5943(10) Å].<sup>50,55,63,64</sup> The  $\mu$ -CO ligand adopts a dissymmetrical position (C1-Fe<sub>2</sub>Cl, 1.788(11); C1-Fe<sub>1</sub>CO, 2.430(12) Å) similar to that observed in analogous dissymmetrical compounds.<sup>55,63,64</sup> The presence of a terminal Cl in [Fe<sub>2</sub>( $\mu$ -SR)<sub>2</sub>L<sub>6</sub>] compounds recalls the structure of rare examples of Fe<sub>2</sub> terminal hydride, which are considered as models of a crucial intermediate in the bidirectional H<sup>+</sup>/H<sub>2</sub> catalytic conversion induced by the H-cluster.<sup>48,63</sup> The spectroscopic measurements recorded in solution, <sup>31</sup>P{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H} NMRs and IR (Fig. S3, S16, S17) accord with the X-ray structural determination of **2**.

In CH<sub>2</sub>Cl<sub>2</sub>, **1** evolves differently than in CHCl<sub>3</sub>, affording the unstable Cl bridged complex [Fe<sub>2</sub>( $\mu$ -pdt)( $\mu$ -Cl)( $\kappa^2$ -dmpe)<sub>2</sub>(CO)<sub>2</sub>]Cl (**3**), after stirring two days at room temperature, with moderate yields (58%). <sup>31</sup>P{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H} NMR and IR spectra of **3** suggest a symmetrical bis-

dibasal geometry (Fig. S3, S19, S20), which is similar to those of analogous complexes  $[\text{Fe}_2(\mu\text{-pdt})(\mu\text{-Cl})(\text{dppR})_2(\text{CO})_2](\text{BF}_4)$  (dppR: dppe, dppv), which have been obtained by assembly of two mono-iron precursors.<sup>47</sup> X-ray quality crystals obtained from a solution containing **3** in  $\text{CH}_2\text{Cl}_2$ : THF mixtures allowed to characterize three complexes consisting in  $[\text{Fe}_2(\mu\text{-pdt})(\mu\text{-Cl})(\kappa^2\text{-dmpe})_2(\text{CO})]^+$  and two mono-iron compounds  $[\text{Fe}(\kappa^2\text{-dmpe})_2(\text{CO})\text{Cl}]^+$  and  $[\text{FeCl}_4]^{2-}$  arising from the decomposition of **3** in solution. Despite the poor crystallographic data, the connectivity of atoms remains without ambiguity, showing the dinuclear structure  $[\text{Fe}_2(\mu\text{-pdt})(\mu\text{-Cl})(\kappa^2\text{-dmpe})_2(\text{CO})]^+$  of **3** (Fig. S1).

Furthermore, the absence of interconversion between **2** and **3** over time is puzzling (Fig. S7, S8). To explore the **2** vs **3** stability and understand how the C-Cl bond activation (induced by **1**) leads to different isomers depending on the activated Cl molecule, a thermodynamic speciation of the Cl species and a mechanistic investigation of their formation were performed by DFT. The most stable Cl isomer resulted the Cl-bridging **3<sub>bb-bb</sub>** (Fig. S26). Other dmpe dispositions are clearly unfavoured. This implies that, starting from **1<sub>ab-ab</sub>**, dmpe ligands must rotate to get **3<sub>bb-bb</sub>**.

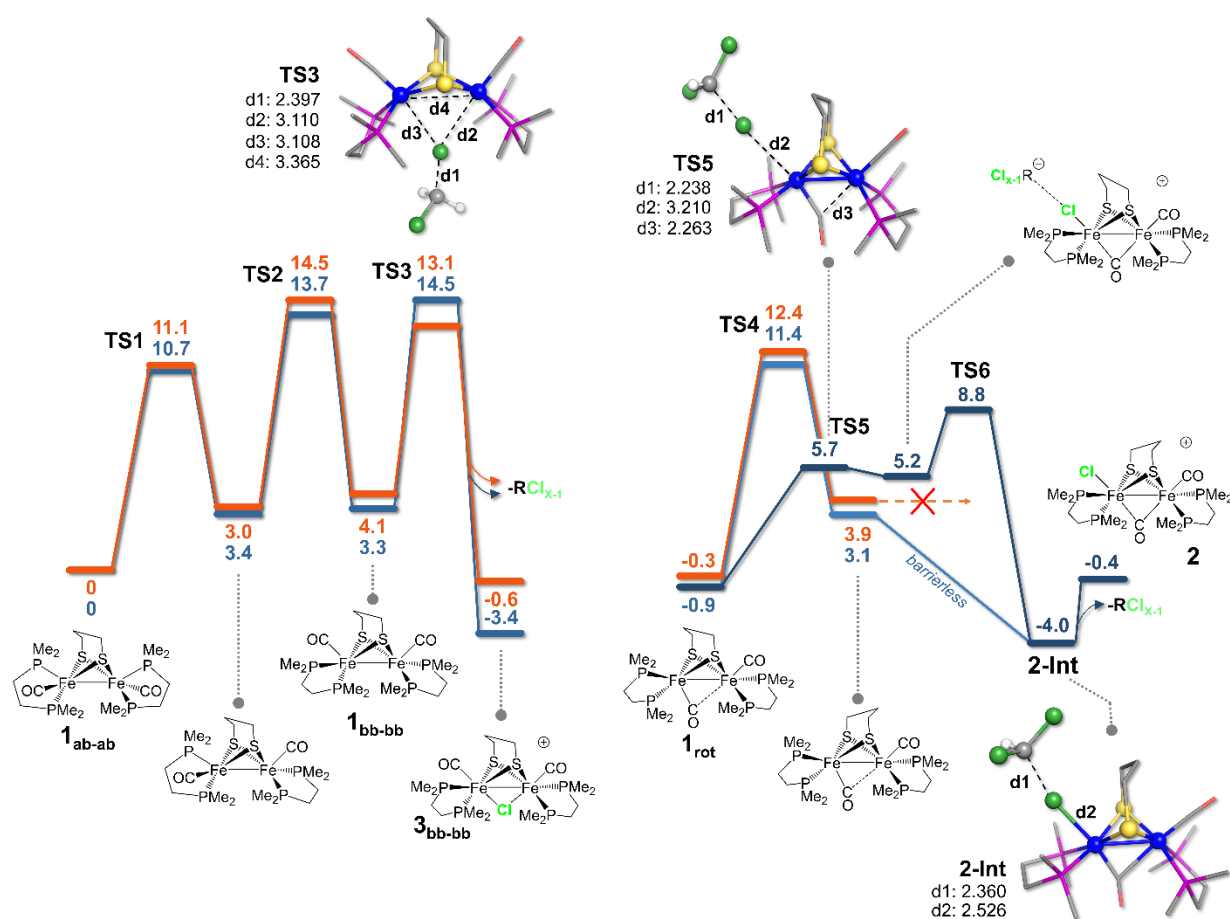
Stable isomers of **2** are also favoured with dmpe ligands in dibasal position but the pdt orientation strongly affects the relative energetic stability (from  $\sim 8.5$  to  $\sim 3$  kcal/mol). Considering the presence of a chelate at the rotating Fe, a Ray-Dutt twist (pseudo-rhombic-tetragonal- rearrangement of four metal ligands in six-coordinated complexes) as a first step of a hypothetical t-Cl/ $\mu$ -Cl interconversion is unlikely since it would bring one of the two P atoms (constrained within the chelate structure) at the Fe-Fe region. The  $\mu$ -Cl/t-Cl interconversion can be conceived as a multi-step mechanism composed by sequential Bailar and Ray-Dutt twists (Fig. S27)<sup>65</sup> that would be thermodynamically feasible ( $\Delta G = \pm 3$

kcal/mol), but kinetically impeded (high activation barriers), irrespective of the solvent considered, in agreement with the observation that **2** and **3** do not interconvert (Scheme 1).

DFT clearly suggests that the reaction mechanism is a direct concerted  $\text{Cl}^+$  transfer, leading to complexes **2** or **3** and a resulting anion  $[\text{RCl}_{x-1}]^-$ . This would subsequently couple to another solvent molecule with concerted  $\text{Cl}^-$  release, a process predicted to be thermodynamically facile, considering its strong exergonicity (-60 kcal/mol for  $\text{CH}_2\text{Cl}_2$  and -48 kcal/mol for  $\text{CHCl}_3$ ), as also confirmed by the experimental evidence. Indeed, the products found in the volatiles of the reaction of **1**+ $\text{CHCl}_3$  confirmed the formation of a  $\text{CHCl}_2^-$  moiety. A mechanism involving an oxidative addition for the activation of the  $\sigma(\text{C}-\text{Cl})$  bond was ruled out due to the high instability of the intermediate species (Fig. S28) and the involvement of a radical  $\text{Fe(I)}(\text{Fe(II)})$  cationic intermediate<sup>66,67</sup> is highly unlikely in reason of the redox behavior of  $\text{CH}_2\text{Cl}_2$ .<sup>68</sup> Sequential ( Fig. 3) and concerted (trimolecular) (Fig. S30) mechanisms, involving one or two solvent molecules, respectively, were finally considered. A kinetic preference for the mechanism with a single solvent molecule was evidenced. The energy profiles for the reaction of **1** with  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  were determined considering the most stable and isoenergetic **1<sub>rot</sub>** and **1<sub>ab-ab</sub>**. DFT suggests that the Cl-bridged **3** could be formed from **1<sub>ab-ab</sub>** both in the presence of  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  (Fig. 3, left) through a  $\text{Cl}^+$  transfer to the Fe-Fe bond only after a preliminary isomerization of **1<sub>ab-ab</sub>** to **1<sub>bb-bb</sub>** (TS1 and TS2), while all other alternatives are unfavored (Fig. S29). The formation of **3<sub>bb-bb</sub>** from **1<sub>bb-bb</sub>** is exergonic both in  $\text{CH}_2\text{Cl}_2$  and in  $\text{CHCl}_3$  with an overall activation barrier of  $\sim 14$  kcal/mol.  $\mu\text{-Cl}$  formation is more favored in  $\text{CHCl}_3$  than in  $\text{CH}_2\text{Cl}_2$  (by  $\sim 3$  kcal/mol) probably due to the higher stability of the anionic  $\text{CHCl}_2^-$  vs  $\text{CH}_2\text{Cl}^-$ , formed upon  $\text{Cl}^+$  transfer. When considering the rotated isomer **1<sub>rot</sub>**, a straight  $\text{Cl}^+$  transfer from  $\text{CHCl}_3$  affords the terminal-Cl complex **2** (Fig. 3, blue



profile) while no  $\text{Cl}^+$  transfer in terminal position is observed with  $\text{CH}_2\text{Cl}_2$  (Fig. 3, orange profile). We ascribe this behavior to the different strength of the C-Cl bond in  $\text{CH}_2\text{Cl}_2$  (BDE = 79 kcal/mol) vs  $\text{CHCl}_3$  (BDE = 72 kcal/mol).<sup>69</sup> Only two pathways lead to **2** from **1**<sub>rot</sub>: the energetically preferred one involves a  $\text{Cl}^+$  transfer (TS5) followed by pdt flip (TS6) to form the most stable isomer of **2**. The overall activation barrier for t-Cl formation is 9.7 kcal/mol, compatible with a fast process even under mild temperature conditions and explains the unique formation of **2** in presence of  $\text{CHCl}_3$ .



**Figure 3.** Free energy profiles (in kcal/mol) for the formation of both **3** and **2**, starting from **1**<sub>ab-ab</sub> (taken as reference) and **1**<sub>rot</sub>, respectively. The structures of intermediates and relevant transition states are reported. Orange profiles are calculated in  $\text{CH}_2\text{Cl}_2$  solvent and in the presence of one explicit  $\text{CH}_2\text{Cl}_2$  molecule ( $\text{R} = \text{CH}_2$ ,  $\text{X} = 2$ ), while blue ones are calculated in  $\text{CHCl}_3$  with an explicit  $\text{CHCl}_3$  molecule ( $\text{R} = \text{CH}$ ,  $\text{X} = 3$ ). The activation barriers for a-b to b-b isomerization of dmpe are taken from reference<sup>40</sup> and have been recalculated in implicit  $\text{CHCl}_3$  solvent. Optimized structures of relevant TS's and intermediates are reported: TS3 for  $\text{CH}_2\text{Cl}_2$ , TS5 and 2-Int for  $\text{CHCl}_3$ . Selected

distances in Å. Atoms coloring: C = grey, Fe = blue, P = purple, S = yellow, O = red, Cl = green, H = white. H atoms of the complex have been omitted for clarity. **2** is only formed in CHCl<sub>3</sub> and the pathway of its formation goes through the 5.7 TS (not found in the CH<sub>2</sub>Cl<sub>2</sub> case). All this implies that **1<sub>rot</sub>** is not a trigger for the stronger C-Cl bond of CH<sub>2</sub>Cl<sub>2</sub> (see BDE values provided in the text), but only for the weaker analog bond of CHCl<sub>3</sub>. On the contrary, in CH<sub>2</sub>Cl<sub>2</sub>, the right-side pathway indicates that **1<sub>rot</sub>** is not a trigger for the C-Cl bond. This is compatible with the slower formation process of **3**, experimentally observed.

## CONCLUSION

In conclusion, the electron-rich **1** is a new example of a 2Fe(I) complex [Fe<sub>2</sub>(μ-pdt)L<sub>x</sub>(CO)<sub>6-x</sub>] for which the coexistence in solution of isoenergetic stereoisomers with unrotated and rotated conformers have been evidenced.<sup>57-59</sup> The control of the unrotated geometry depends on diiron redox state and is still challenging. It remains a crux for having a hydrogenase-like activity.<sup>70,71</sup> Moreover, the reactivity of **1** towards CH<sub>x</sub>Cl<sub>4-x</sub> (x = 1, 2) compounds is an original example of bimetallic activation of robust C-Cl bonds at a {Fe<sub>2</sub>S<sub>2</sub>} site that leads to terminal or bridged Cl isomers, which may arise through a concerted regiochemically selective (FeFe site vs Fe apical regions) formal transfer of chloronium. This depends on the unrotated or rotated conformation of **1** and the relative stability of the generated anion CH<sub>x</sub>Cl<sub>3-x</sub><sup>-</sup> (x = 1, 2). Finally, these results could be relevant to the treatment and degradation of halogenated organic pollutants. Further investigations on the reactivity of **1** towards other environmentally relevant chlorinated molecules are under way.

## ASSOCIATED CONTENT

### Supporting Information.

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem>.

Protocols for syntheses, NMR, IR, ESI spectra of products, crystallographic and DFT data (DOC)

CCDC 2246265-2246266, 2281641 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk\\_request/cif](http://www.ccdc.cam.ac.uk_request/cif)

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### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### **Funding Sources**

The research was supported by ANR funding: JCJC OxySplit-H2 (ANR-20-CE07-0027-01).

### **Notes**

### **ACKNOWLEDGMENT**

We are grateful to the ‘Service Général des Plateformes, Brest’ for NMR experiments and XRD recordings. L. C. is grateful to Dr. J. Pécaut for the help in the crystallographic structure resolution. L.C. thanks the ANR (Agence Nationale de Recherche) for funding the project JCJC OxySplit-H2 (ANR-20-CE07-0027-01).

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§ These values have been calculated using a “simplified” approach according to the equations:  $\Delta G = G(\text{C}_2\text{H}_2\text{Cl}_4) + G(\text{Cl}^-) - G(\text{CHCl}_2^-) - G(\text{CHCl}_3)$  and  $\Delta G = G(\text{C}_2\text{H}_4\text{Cl}_2) + G(\text{Cl}^-) - G(\text{CH}_2\text{Cl}^-) - G(\text{CH}_2\text{Cl}_2)$ , considering each molecule at infinite distance with respect to the others. Although probably underestimated, these values are compatible with a strongly favored process and with a higher reactivity of  $\text{CH}_2\text{Cl}^-$  vs  $\text{CHCl}_3^-$ .

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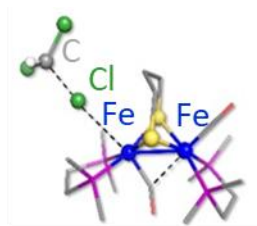
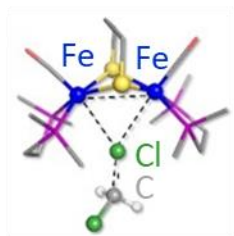
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## Table of content SYNOPSIS



Regioselective chloronium transfer  
at rotated or unrotated diiron isomers

An unprecedented bimetallic activation of C-Cl bonds in small chlorinated organic molecules at an electron-rich dithiolate dinuclear site, related to the H-cluster, arises from the cleavage of C-Cl bonds and formal regioselective chloronium transfer.