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

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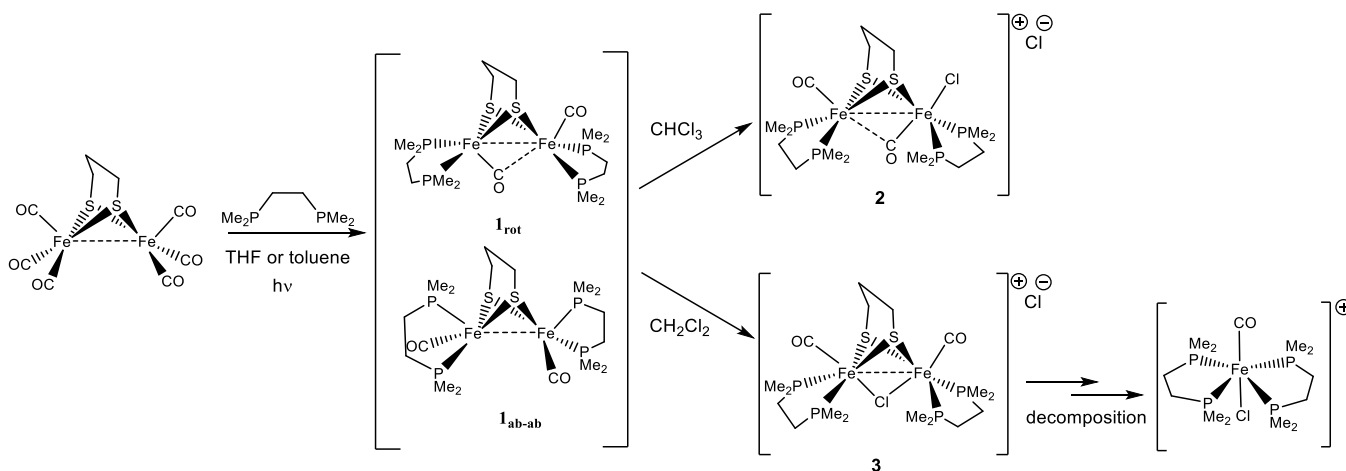
ABSTRACT

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.¹⁻¹⁰ While numerous mononuclear complexes able to activate small $\text{CH}_x\text{Cl}_{4-x}$ ($x = 1, 2$) substrates have been reported,¹¹⁻¹⁵ well-defined polymetallic complexes (generally based on 2nd-3rd row transition metals), which induce

the cleavage of C-Cl bonds of polychlorinated molecules, are more scarce.^{16–30} 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⁺/H₂ conversion,^{31–40} has been little explored.^{41–46} The activation of chlorinated organic molecules with such Fe₂ complexes has never been reported. Here we present the reactivity towards polychlorinated molecules of the bis-chelated complex $[\text{Fe}_2(\mu\text{-pdt})(\kappa^2\text{-dmpe})_2(\text{CO})_2]$ (**1**) (dmpe: 1,2-bis(dimethylphosphino)ethane; pdt: propanedithiolate), a new example of tetrasubstituted diiron dithiolate complex.^{47–55} 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 $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$, 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 $[\text{Fe}_2(\mu\text{-SR})_2\text{L}_6]$

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

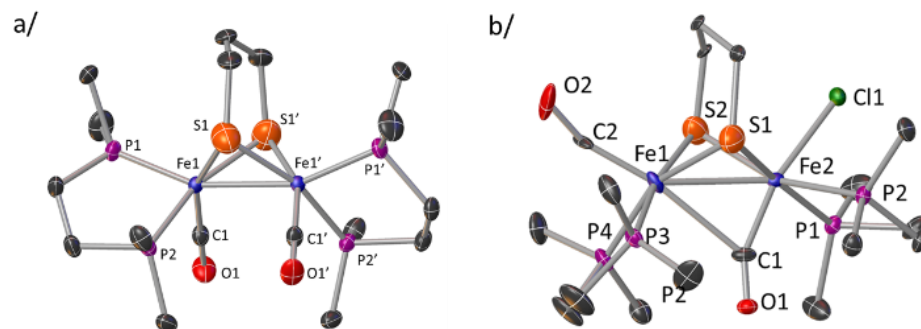


Figure 1 Crystallographic structures of **a/** $[\text{Fe}_2(\mu\text{-pdt})(\kappa^2\text{-dmpe})_2(\text{CO})_2]$ (**1**). Atoms labeled with 'are obtained with a 2-fold axis ($1-x, +y, \frac{1}{2}-z$); **b/** $[\text{Fe}_2(\mu\text{-pdt})(\mu\text{-CO})(\kappa^2\text{-dmpe})_2(\text{CO})\text{Cl}]\text{Cl}\cdot 4\text{CHCl}_3$ (**2.4CHCl₃**). Displacement ellipsoids are drawn at the 40% probability level and disorders, CHCl_3 solvent molecules, Cl^- counter ion and hydrogen atoms are omitted for clarity

The ^1H NMR spectrum of a freshly prepared solution of **1** in CD_2Cl_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 CD_2Cl_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 CD_2Cl_2 , this signal splits into two singlets at 69.1 and 52.3 ppm (Fig. S10), which could be attributed to the isomer **1_{ab-ab}** observed in solid state. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 203K in CD_2Cl_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_{ab-ab}**. In C_6D_6 and 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 cm^{-1} (Fig. S5) which are, as expected, shifted to lower frequencies compared to those of its dppv (cis-1,2-bis(diphenylphosphino)ethylene) analog⁵¹ and very close to that of $[\text{Fe}_2(\mu\text{-pdt})(\text{PMe}_3)_4(\text{CO})_2]$.⁴⁸ Unlike these latter four-substituted compounds, a third weak band lies at 1799 cm^{-1} in the range of $\nu(\mu\text{-CO})$ bands.^{57–59} To gain further insights into the isomeric stability, a thermodynamic speciation of **1** was carried out by DFT in both CH_2Cl_2 and CHCl_3 solvents (Fig. 2 and ESI-section VI).^{60–62} Two isoenergetic structures were found as the most stable: a bis-(apical-basal) unrotated isomer **1_{ab-ab}**, that resembles the X-ray structure of **1**, and unexpectedly, a bis-(dibasal) rotated form (**1_{rot}**). The DFT IR $\nu(\text{CO})$ s suggest that the three bands experimentally observed (1795, 1836 and 1856 cm^{-1} in CH_2Cl_2) likely arise from an equilibrium mixture of these two low-energy isomers in solution. Specifically, the band at 1795 cm^{-1} can be assigned to the semi-bridging CO in **1_{rot}**. No other rotated isomer was found as stable structure. Moreover, calculated ^{31}P NMR chemical shifts of **1_{ab-ab}** and **1_{rot}** agree with experimental observations (Fig. S25).

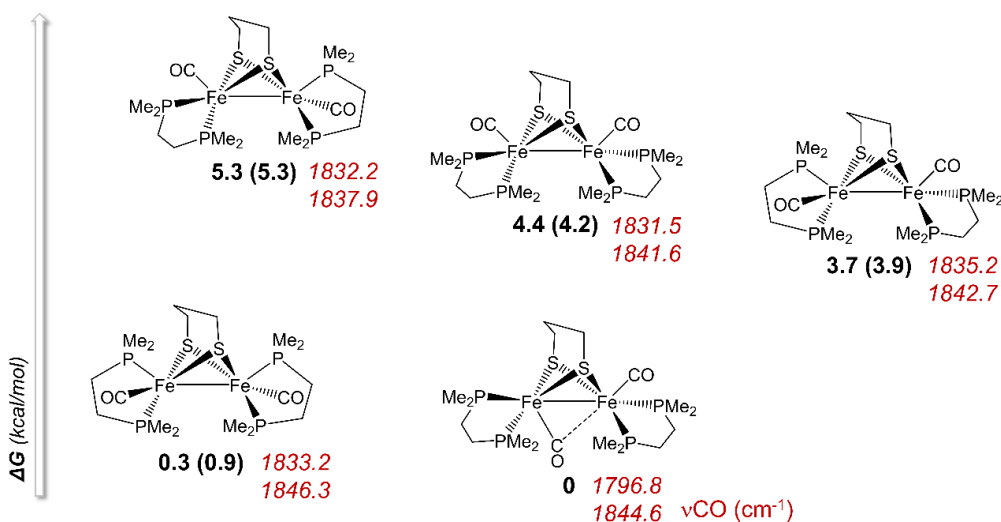


Figure 2. Thermodynamic speciation of **1**. Relative free energies (kcal/mol) in CH₂Cl₂ and CHCl₃ (in parenthesis) and $\nu(\text{CO})$ s (cm⁻¹, gas phase, red values) are reported.

The dissolution of **1** into CHCl₃ (experiments performed both in light and in dark to prevent the formation of halocarbon radicals) afforded serendipitously X-ray quality crystals of [Fe₂(μ -pdt)(μ -CO)(κ^2 -dmpe)₂(CO)Cl]Cl·4CHCl₃ **2**·4(CHCl₃) (Fig. 1b). **2** could be readily and quantitatively prepared, at room temperature, by addition of a drop of CHCl₃ 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 CH₂Cl₂, C₂H₂Cl₄, C₂HCl₃ (ESI-Section VII). The X-ray structure of **2** reveals a cationic {Fe₂S₂} 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].^{50,55,63,64} The μ -CO ligand adopts a dissymmetrical position (C1-Fe₂Cl, 1.788(11); C1-Fe₁CO, 2.430(12) Å) similar to that observed in analogous dissymmetrical compounds.^{55,63,64} The presence of a terminal Cl in [Fe₂(μ -SR)₂L₆] compounds recalls the structure of rare examples of Fe₂ terminal hydride, which are considered as models of a crucial intermediate in the bidirectional H⁺/H₂ catalytic conversion induced by the H-cluster.^{48,63} The spectroscopic measurements recorded in solution, ³¹P{¹H}, ¹³C{¹H} NMRs and IR (Fig. S3, S16, S17) accord with the X-ray structural determination of **2**.

In CH₂Cl₂, **1** evolves differently than in CHCl₃, affording the unstable Cl bridged complex [Fe₂(μ -pdt)(μ -Cl)(κ^2 -dmpe)₂(CO)₂]Cl (**3**), after stirring two days at room temperature, with moderate yields (58%). ³¹P{¹H}, ¹³C{¹H} 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.⁴⁷ X-ray quality crystals obtained from a solution containing **3** in CH_2Cl_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_{bb-bb}** (Fig. S26). Other dmpe dispositions are clearly unfavoured. This implies that, starting from **1_{ab-ab}**, dmpe ligands must rotate to get **3_{bb-bb}**.

Stable isomers of **2** are also favoured with dmpe ligands in dibasal position but the pdt orientation strongly affects the relative energetic stability (from ~ 8.5 to ~ 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/ μ -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 μ -Cl/t-Cl interconversion can be conceived as a multi-step mechanism composed by sequential Bailar and Ray-Dutt twists (Fig. S27)⁶⁵ 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 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 Cl^- release, a process predicted to be thermodynamically facile, considering its strong exergonicity (-60 kcal/mol for CH_2Cl_2 and -48 kcal/mol for CHCl_3), as also confirmed by the experimental evidence. Indeed, the products found in the volatiles of the reaction of **1**+ CHCl_3 confirmed the formation of a 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^{66,67} is highly unlikely in reason of the redox behavior of CH_2Cl_2 .⁶⁸ 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 CH_2Cl_2 and CHCl_3 were determined considering the most stable and isoenergetic **1_{rot}** and **1_{ab-ab}**. DFT suggests that the Cl-bridged **3** could be formed from **1_{ab-ab}** both in the presence of CH_2Cl_2 or CHCl_3 (Fig. 3, left) through a Cl^+ transfer to the Fe-Fe bond only after a preliminary isomerization of **1_{ab-ab}** to **1_{bb-bb}** (TS1 and TS2), while all other alternatives are unfavored (Fig. S29). The formation of **3_{bb-bb}** from **1_{bb-bb}** is exergonic both in CH_2Cl_2 and in CHCl_3 with an overall activation barrier of ~ 14 kcal/mol. $\mu\text{-Cl}$ formation is more favored in CHCl_3 than in CH_2Cl_2 (by ~ 3 kcal/mol) probably due to the higher stability of the anionic CHCl_2^- vs CH_2Cl^- , formed upon Cl^+ transfer. When considering the rotated isomer **1_{rot}**, a straight Cl^+ transfer from CHCl_3 affords the terminal-Cl complex **2** (Fig. 3, blue

profile) while no Cl^+ transfer in terminal position is observed with CH_2Cl_2 (Fig. 3, orange profile). We ascribe this behavior to the different strength of the C-Cl bond in CH_2Cl_2 (BDE = 79 kcal/mol) vs CHCl_3 (BDE = 72 kcal/mol).⁶⁹ Only two pathways lead to **2** from **1**_{rot}: the energetically preferred one involves a 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 CHCl_3 .

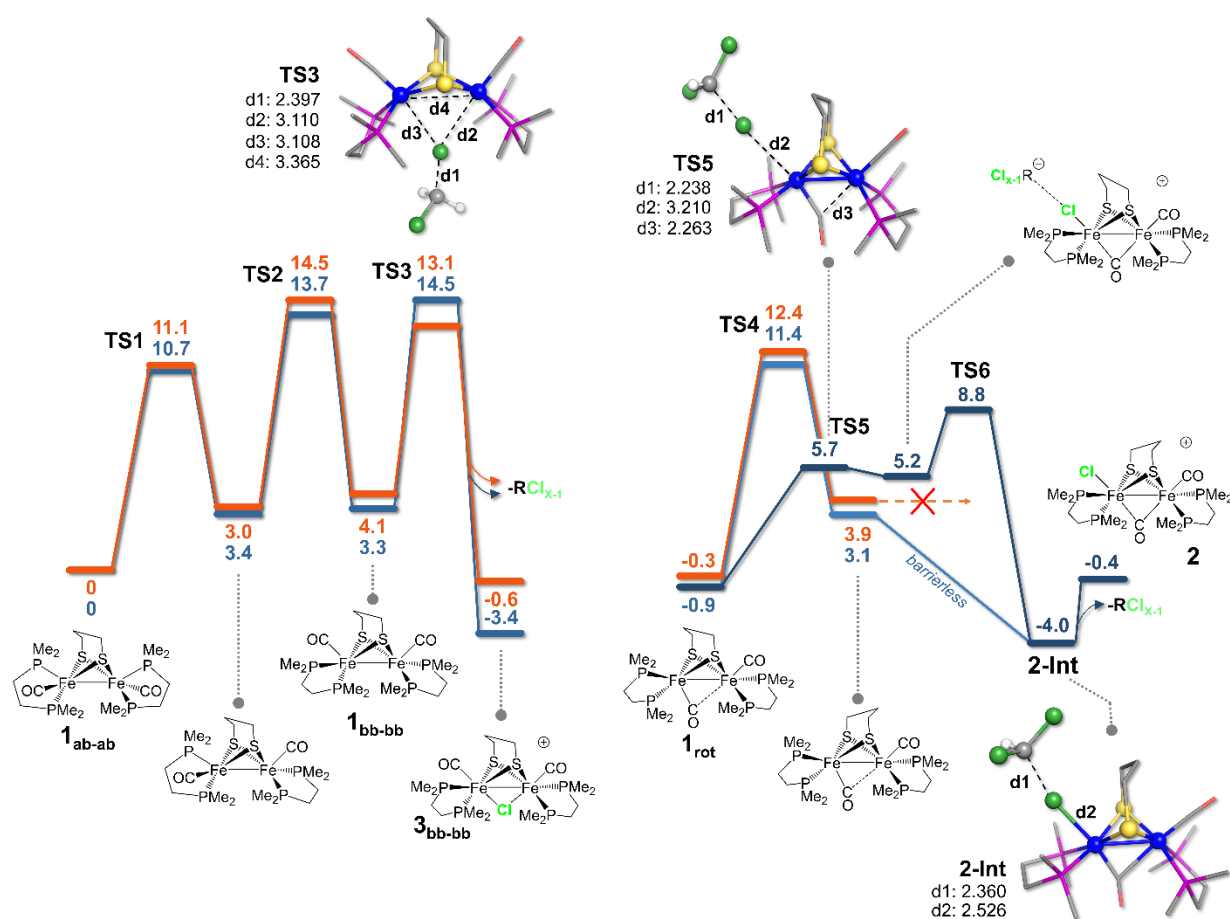


Figure 3. Free energy profiles (in kcal/mol) for the formation of both **3** and **2**, starting from **1**_{ab-ab} (taken as reference) and **1**_{rot}, respectively. The structures of intermediates and relevant transition states are reported. Orange profiles are calculated in CH_2Cl_2 solvent and in the presence of one explicit CH_2Cl_2 molecule ($\text{R} = \text{CH}_2$, $\text{X} = 2$), while blue ones are calculated in CHCl_3 with an explicit 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 reference⁴⁰ and have been recalculated in implicit CHCl_3 solvent. Optimized structures of relevant TS's and intermediates are reported: TS3 for CH_2Cl_2 , TS5 and 2-Int for 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 CHCl₃ and the pathway of its formation goes through the 5.7 TS (not found in the CH₂Cl₂ case). All this implies that **1_{rot}** is not a trigger for the stronger C-Cl bond of CH₂Cl₂ (see BDE values provided in the text), but only for the weaker analog bond of CHCl₃. On the contrary, in CH₂Cl₂, the right-side pathway indicates that **1_{rot}** 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 [Fe₂(μ-pdt)L_x(CO)_{6-x}] for which the coexistence in solution of isoenergetic stereoisomers with unrotated and rotated conformers have been evidenced.⁵⁷⁻⁵⁹ 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.^{70,71} Moreover, the reactivity of **1** towards CH_xCl_{4-x} (x = 1, 2) compounds is an original example of bimetallic activation of robust C-Cl bonds at a {Fe₂S₂} 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_xCl_{3-x}⁻ (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

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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.

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Notes

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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 CH_2Cl^- vs CHCl_3^- .

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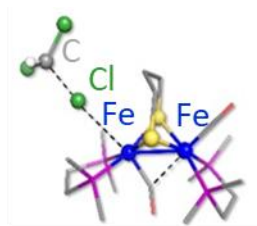
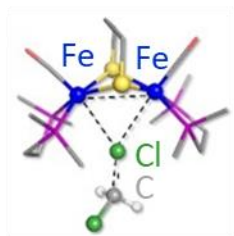
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Table of content SYNOPSIS



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.