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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, $[Fe_2(\mu-pdt)(\kappa^2-dmpe)_2(CO)_2]$ (**1**), is highly reactive towards chlorinated compounds CH_xCl_{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 CH_xCl_{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 [Fe₂(μ -pdt)(κ^2 -dmpe)₂(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 $[Fe_2(\mu-pdt)(CO)_6]$, 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 $[Fe_2(\mu-SR)_2L_6]$

compounds with a butterfly $\{Fe_2S_2\}$ 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**/ $[Fe_2(\mu-pdt)(\kappa^2-dmpe)_2(CO)_2]$ (**1**). Atoms labeled with 'are obtained with a 2-fold axis (1-x, +y, ½-z)); **b**/ $[Fe_2(\mu-pdt)(\mu-CO)(\kappa^2-dmpe)_2(CO)CI]CI.4CHCI_3$ (**2**.4CHCI₃). Displacement ellipsoids are drawn at the 40% probability level and disorders, CHCI₃ solvent molecules, Cl⁻ counter ion and hydrogen atoms are omitted for clarity

The ¹H NMR spectrum of a freshly prepared solution of **1** in CD₂Cl₂ showed ill-resolved resonances between 2.27 and 1.42 ppm assigned to the signals of both dmpe and pdt ligands (Fig. S9). The ³¹P{¹H} NMR spectrum of **1** in CD₂Cl₂ 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 CD₂Cl₂, 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. ¹³C{¹H} NMR spectrum at 203K in CD₂Cl₂ (Fig. S12) confirms the symmetry of **1**. It is noteworthy that depending on the solvent, further resonances were detected in the ³¹P{¹H} NMR spectrum in addition to the broad signal of **1**, which suggests the presence in solution of an isomer **1**_{ab-ab}. In C₆D₆ and THF-D₈ 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 v(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-1,2bis(diphenylphosphino)ethylene) analog⁵¹ and very close to that of $[Fe_2(\mu$ pdt)(PMe₃)₄(CO)₂].⁴⁸ Unlike these latter four-substituted compounds, a third weak band lies at 1799 cm⁻¹ in the range of $v(\mu$ -CO) bands.^{57–59} To gain further insights into the isomeric stability, a thermodynamic speciation of $\mathbf{1}$ was carried out by DFT in both CH_2Cl_2 and CHCl₃ solvents (Fig. 2 and ESI-section VI).^{60–62} Two isoenergetic structures were found as the most stable: a bis-(apical-basal) unrotated isomer $\mathbf{1}_{ab-ab}$, that resembles the X-ray structure of 1, and unexpectedly, a bis-(dibasal) rotated form (1_{rot}) . The DFT IR vCO)s suggest that the three bands experimentally observed (1795, 1836 and 1856 cm⁻¹ in CH₂Cl₂) 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 ³¹P NMR chemical shifts of $\mathbf{1}_{ab-ab}$ and $\mathbf{1}_{rot}$ agree with experimental observations (Fig. S25).



Figure 2. Thermodynamic speciation of **1**. Relative free energies (kcal/mol) in CH₂Cl₂ and CHCl₃ (in parenthesis) and v(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 $[Fe_2(\mu-pdt)(\mu-CO)(\kappa^2-dmpe)_2(CO)CI]CI.4CHCl_3$ **2**.4(CHCl_3) (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 diferrous 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-Fe2_{cl}, 1.788(11); C1-Fe1_{co}, 2.430(12) Å) similar to that observed in analogous dissymmetrical compounds.^{55,63,64} The presence of a terminal CI in $[Fe_2(\mu-SR)_2L_6]$ 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 CI bridged complex $[Fe_2(\mu-pdt)(\mu-CI)(\kappa^2-dmpe)_2(CO)_2]CI$ (**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 $[Fe_2(\mu-pdt)(\mu-Cl)(dppR)_2(CO)_2](BF_4)$ (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 CH₂Cl₂: THF mixtures allowed to characterize three complexes consisting in $[Fe_2(\mu-pdt)(\mu-Cl)(\kappa^2-dmpe)_2(CO)]^+$ and two mono-iron compounds $[Fe(\kappa^2-dmpe)_2(CO)Cl]^+$ and $[FeCl_4]^{2-}$ arising from the decomposition of **3** in solution. Despite the poor crystallographic data, the connectivity of atoms remains without ambiguity, showing the dinuclear structure $[Fe_2(\mu-pdt)(\mu-Cl)(\kappa^2-dmpe)_2(CO)]^+$ 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 hypothetic 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 $[RCl_{x-1}]^{-1}$. 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 CH₂Cl₂ and -48 kcal/mol for CHCl₃), as also confirmed by the experimental evidence. Indeed, the products found in the volatiles of the reaction of 1+CHCl₃ confirmed the formation of a CHCl₂⁻ moiety. A mechanism involving an oxidative addition for the activation of the σ (C-Cl) bond was ruled out due to the high instability of the intermediate species (Fig. S28) and the involvement of a radical Fe(I)(Fe(II) cationic intermediate^{66,67} is highly unlikely in reason of the redox behavior of CH₂Cl₂.⁶⁸ 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 $\mathbf{1}$ with CH₂Cl₂ and CHCl₃ were determined considering the most stable and isoenergetic $\mathbf{1}_{rot}$ and $\mathbf{1}_{ab-ab}$. DFT suggests that the Cl-bridged **3** could be formed from $\mathbf{1}_{ab-ab}$ both in the presence of CH₂Cl₂ or CHCl₃ (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 $\mathbf{3}_{bb-bb}$ from $\mathbf{1}_{bb-bb}$ is exergonic both in CH₂Cl₂ and in CHCl₃ with an overall activation barrier of ~14 kcal/mol. μ -Cl formation is more favored in CHCl₃ than in CH₂Cl₂ (by ~3 kcal/mol) probably due to the higher stability of the anionic CHCl₂⁻ vs CH₂Cl⁻, formed upon Cl⁺ transfer. When considering the rotated isomer 1_{rot}, a straight Cl⁺ transfer from CHCl₃ affords the terminal-Cl complex 2 (Fig. 3, blue

profile) while no Cl⁺ transfer in terminal position is observed with CH₂Cl₂ (Fig. 3, orange profile). We ascribe this behavior to the different strength of the C-Cl bond in CH₂Cl₂ (BDE = 79 kcal/mol) vs CHCl₃ (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 CHCl₃.



Figure 3. Free energy profiles (in kcal/mol) for the formation of both **3** and **2**, starting from $\mathbf{1}_{ab-ab}$ (taken as reference) and $\mathbf{1}_{rot}$, respectively. The structures of intermediates and relevant transition states are reported. Orange profiles are calculated in CH₂Cl₂ solvent and in the presence of one explicit CH₂Cl₂ molecule (R = CH₂, X = 2), while blue ones are calculated in CHCl₃ with an explicit CHCl₃ molecule (R = CH, X = 3). The activation barriers for a-b to b-b isomerization of dmpe are taken from reference⁴⁰ and have been recalculated in implicit CHCl₃ solvent. Optimized structures of relevant TS's and intermediates are reported: TS3 for CH₂Cl₂, TS5 and 2-Int for CHCl₃. 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 $\mathbf{1}_{rot}$ 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 $\mathbf{1}_{rot}$ 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 $[Fe_2(\mu-pdt)L_x(CO)_{6-x}]$ 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

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Notes

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§ These values have been calculated using a "simplified" approach according to the equations: $\Delta G = G(C_2H_2CI_4) + G(CI^{-}) - G(CHCI_2^{-}) - G(CHCI_3)$ and $\Delta G = G(C_2H_4CI_2) + G(CI^{-}) - G(CH_2CI_2)$, 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_2CI^{-} vs $CHCI_3^{-}$.

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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.