

Density functional calculations show noncovalent interactions driving electrocatalysis



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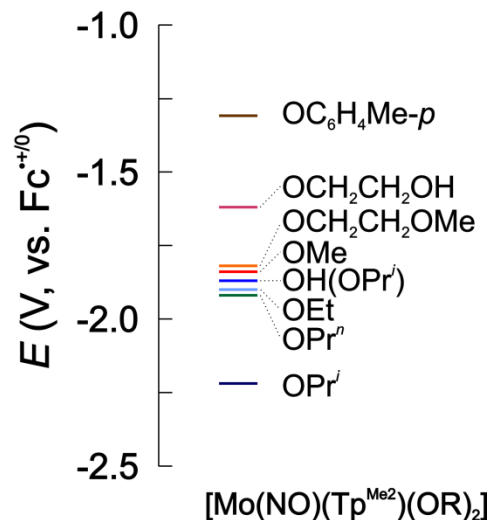
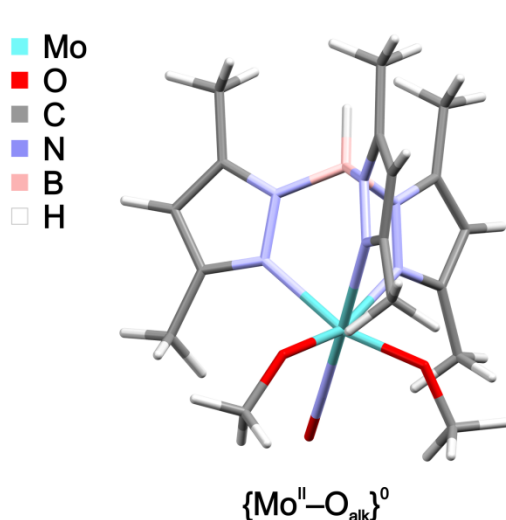
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Scientific interests

- Electron transfer mechanism between redox centres in mixed-valence molybdenum and tungsten scorpionates involved in electrocatalysis
- Dissociative electron transfer (DET) processes in dehalogenation of organic halides
- Role of noncovalent interactions in electrocatalysis and DET processes
- Computational estimation of reduction and oxidation potentials of transition metal complexes and organic compounds

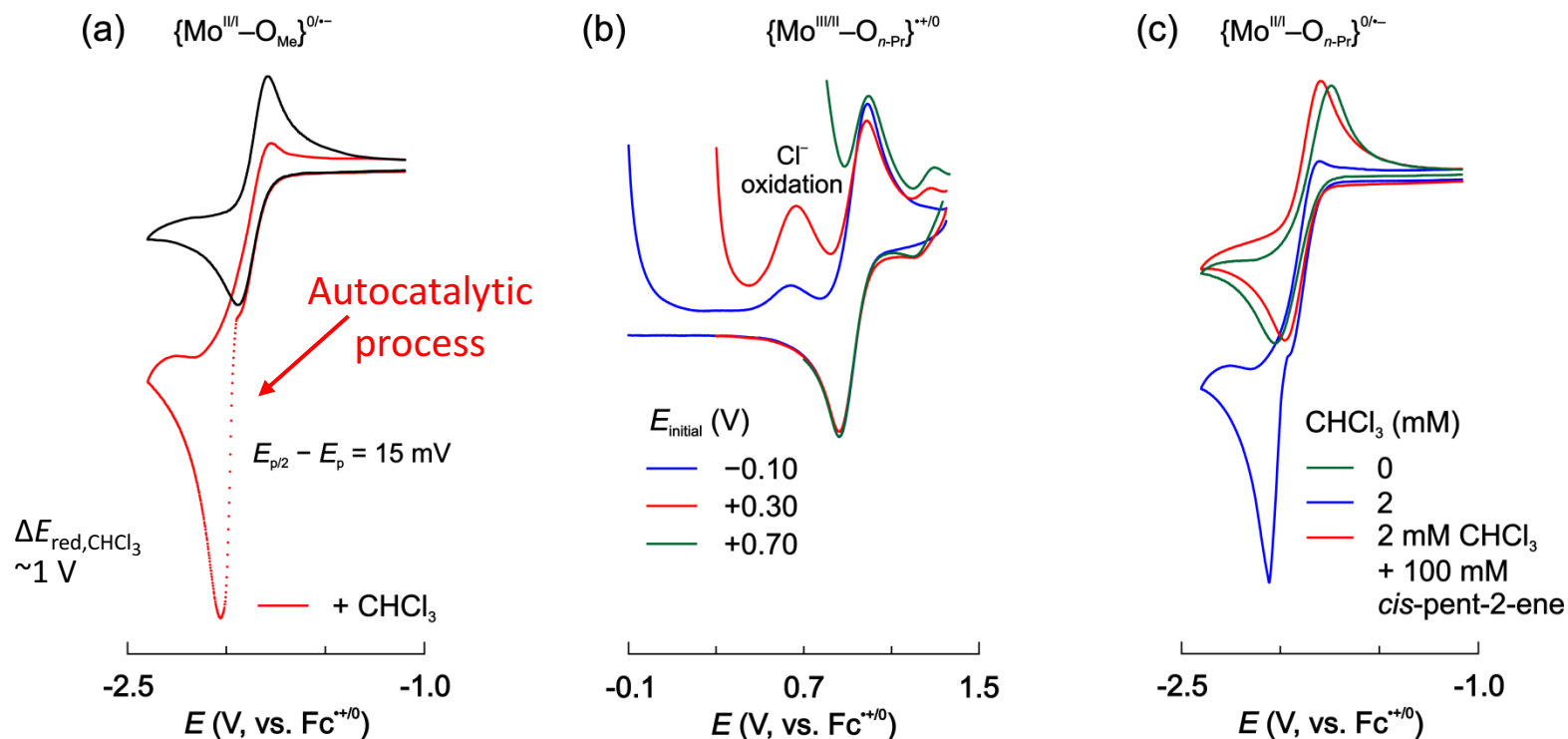
Mo and W scorpionate alkoxides



Reversible redox potential fine tuned by alkoxy ligand RO⁻

- Redox potential of $\{\text{M}^{\text{II/I}}(\text{NO})(\text{Tp}^{\text{Me}_2})-\text{O}_{\text{alk}}\}^{0/\bullet-}$ (M = Mo or W) well reproduced by DFT:B3LYP/LACV3P+/ IEF-PCM:
 - $\{\text{Mo}-\text{O}_{\text{Me}}\}^{0/\bullet-}$ - calculated: 1.80 V, measured: 1.84 V
 - $\{\text{W}-\text{O}_{\text{Me}}\}^{0/\bullet-}$ - calculated: 2.45 V, measured: 2.40 V
- Strong metal-metal interactions (up to $\Delta_{\text{red}} E_{1/2}$ 1440 mV) in mixed-valence compounds with two $\{\text{Mo}^{\text{II-0}}(\text{NO}^+)(\text{Tp}^{\text{Me}_2})\}^{2+,1+,0}$ cores

Electrocatalysis of CHCl_3 dehalogenation by $\{\text{Mo}^{\text{I}}(\text{NO})(\text{Tp}^{\text{Me}_2})(\text{O}_{\text{alkoxy}})\}^{\bullet-}$



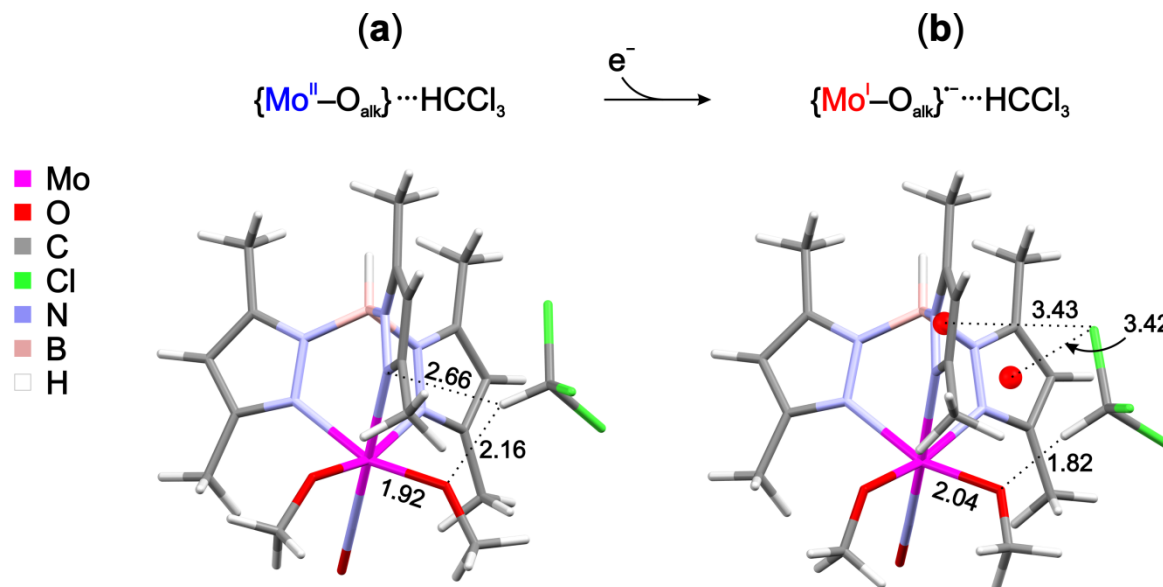
Reduction of CHCl_3 by $\{\text{Mo}^{\text{I}}(\text{NO})(\text{Tp}^{\text{Me}_2})(\text{O}_{\text{alkoxy}})\}^{\bullet-}$

Hold-ramp-step experiment proving stability of catalyst

Inhibition of reaction by alkene

- CHCl_3 - fast autocatalytic process
- CCl_4 and C_2Cl_4 do not react in those conditions, C_2HCl_5 and C_2HCl_3 - typical electrocatalysis

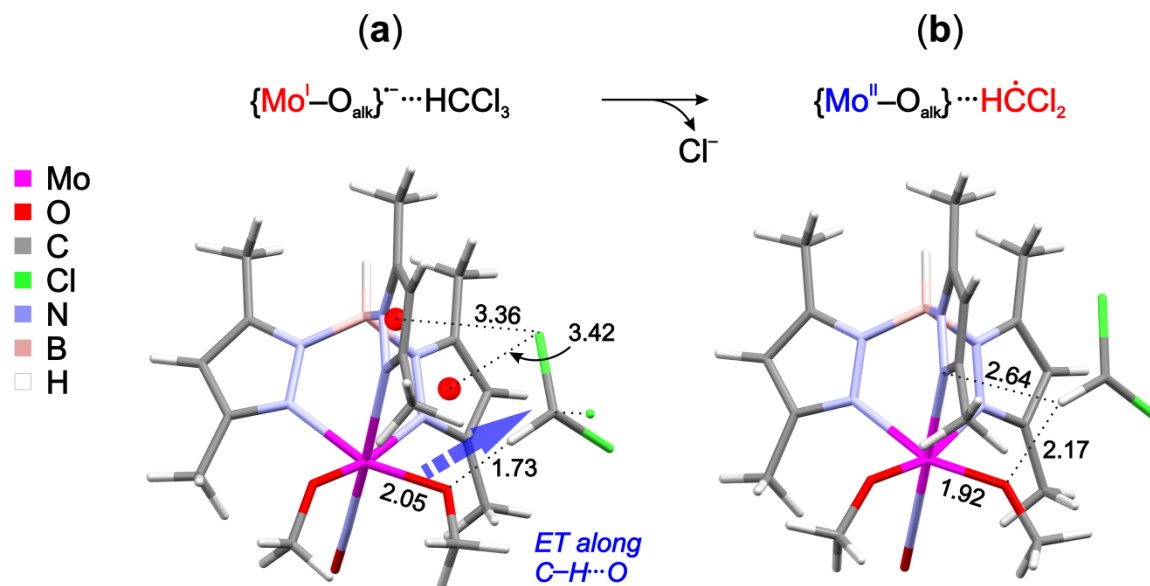
Role of $\{\text{Mo}^{\text{II/I}}(\text{NO})(\text{Tp}^{\text{Me}_2})(\text{O}_{\text{alkoxy}})\}^{\bullet-}$ in electrocatalysis - adducts



DFT-D (COSMO/B3LYP-D3/def2-TZVPP) geometries of $\{\text{Mo}^{\text{II/I}}(\text{NO})(\text{Tp}^{\text{Me}_2})\}(\text{OCH}_3)_2$ adducts with CHCl_3

- Mo scorpionates form weakly bonded adducts with CHCl_3 through $\text{C}-\text{H} \cdots \text{O}_{\text{alkoxy}}$ hydrogen bond and dispersive interactions
- After reduction of Mo centre ΔE_{bind} increases

Role of $\{\text{Mo}^{\text{I/II}}(\text{NO})(\text{Tp}^{\text{Me}_2})(\text{O}_{\text{alkoxy}})\}^{\bullet-}$ in electrocatalysis - dehalogenation



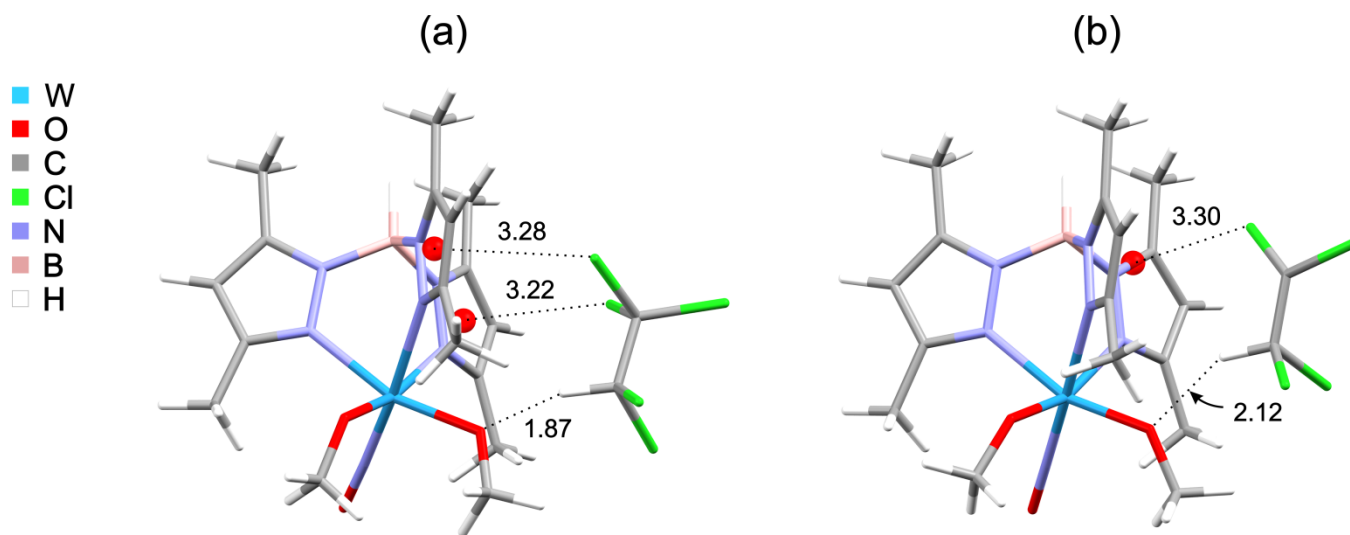
DFT-D (COSMO/B3LYP-D3/def2-TZVPP) geometries of

(a) $\{\text{Mo}^{\text{I}}(\text{NO})(\text{Tp}^{\text{Me}_2})\}(\text{OCH}_3)_2^{\bullet-} \cdots \text{HCCl}_3$ adduct with elongated C-Cl bond (up to 2.2 Å) in CHCl_3

(b) $\{\text{Mo}^{\text{II}}(\text{NO})(\text{Tp}^{\text{Me}_2})\}(\text{OCH}_3)_2 \cdots \text{HCCl}_2^{\bullet}$ adduct after DET

- Weakly bonded $\{\text{Mo}^{\text{I}}(\text{NO})(\text{Tp}^{\text{Me}_2})\}(\text{OCH}_3)_2^{\bullet-} \cdots \text{HCCl}_3$ adduct facilitates electron transfer to chloroform coupled with C-Cl bond cleavage

Role of $\{W^{II/I}(NO)(Tp^{Me_2})(O_{alkoxy})\}^{\bullet-}$ in C_2HCl_5 and $C_2HCl_4^{\bullet}$ dehalogenation



DFT-D (COSMO/B3LYP-D3/def2-TZVPP) geometries of
 (a) $\{W^I(NO)(Tp^{Me_2})\}(OCH_3)_2^{\bullet-} \cdots HC_2Cl_5$ adduct
 (b) $\{W^{II}(NO)(Tp^{Me_2})\}(OCH_3)_2 \cdots HC_2Cl_4^{\bullet}$ adduct after DET

- Weakly bonded $\{W^I(NO)(Tp^{Me_2})\}(OCH_3)_2^{\bullet-} \cdots HC_2Cl_5$ adduct also facilitates electron transfer to pentachloroethane coupled with C-Cl bond cleavage

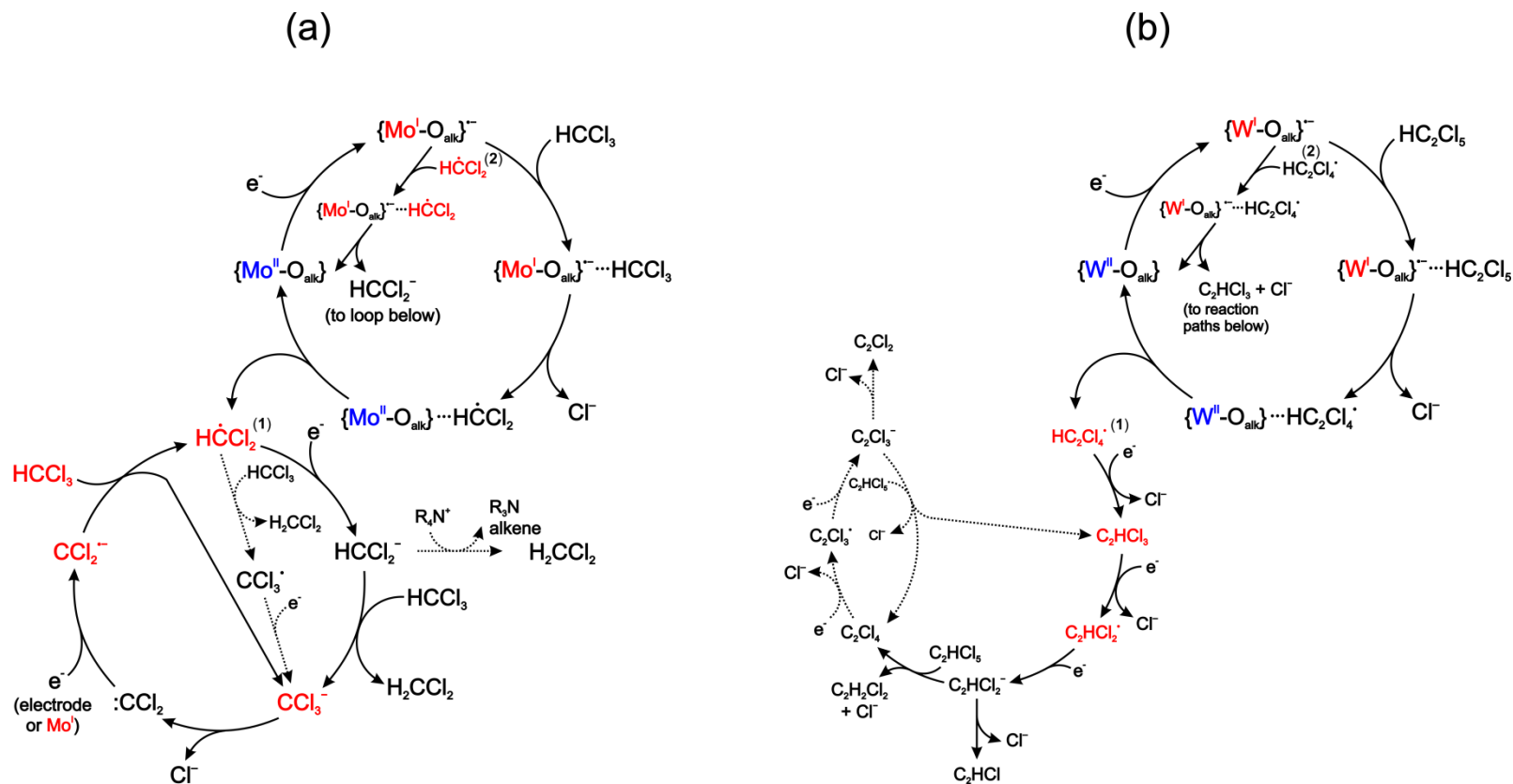
Thermodynamical stability of adducts

Adduct	ΔE_{bind}	ΔG_{bind}
$\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\}^0 \cdots \text{HCCl}_3$	-44.4	0.8
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_3$	-52.3	-6,7
$\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\}^0 \cdots \text{HCCl}_2^{\bullet}$	-37.2	6.3
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_5$	-53.6	-2.9
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_3$	-43.1	1.3
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{H}_2\text{CCl}_2$	-37.7	3.8
$\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_5$	-54.8	-5.0
$\{\text{W}^{\text{II}}-\text{O}_{\text{alk}}\} \cdots \text{HC}_2\text{Cl}_4^{\bullet}$	-46.4	1.7
$\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_4^{\bullet}$	-56.1	-5.4
$\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_3$	-44.4	0.4
$\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{H}_2\text{CCl}_2$	-41.0	1.7

in $\text{kJ}\cdot\text{mol}^{-1}$ in CH_2Cl_2 solvent, BSSE corrected

- $\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_3$ and $\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC}_2\text{Cl}_5$ stabilisation facilitates ET
- Lower stability of $\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\}^0 \cdots \text{HCCl}_2^{\bullet}$ and $\{\text{W}^{\text{II}}-\text{O}_{\text{alk}}\} \cdots \text{HC}_2\text{Cl}_4^{\bullet}$ enables radical dissociation and triggers another catalytic loop

Molecular catalysis of CHCl_3 and C_2HCl_3 reduction triggered by Mo/W alkoxy scorpionates



- CHCl_3 dehalogenation - two catalytic loops, with autocatalytic reaction:

$$2\text{CHCl}_3 + \text{CCl}_2^{\bullet-} + 3e^- \rightarrow \text{CH}_2\text{Cl}_2 + 2\text{CCl}_2^{\bullet-} + 2\text{Cl}^-$$
- For C_2HCl_3 even more cathodic $\text{W}^{\text{II/I}}$ redox potential not sufficient to close second organic loop

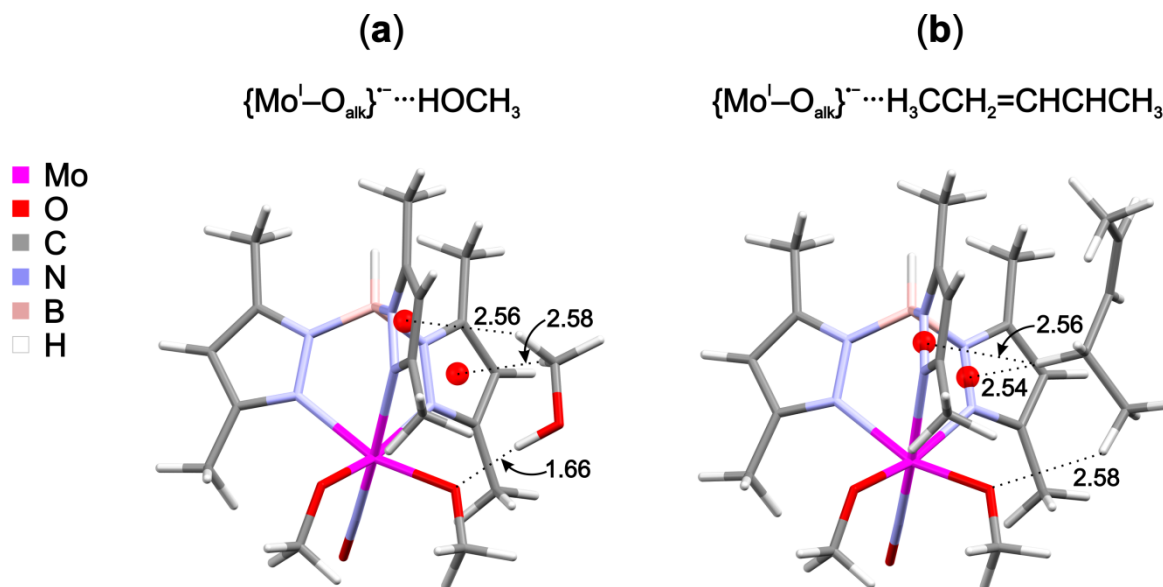
Redox potentials of compounds involved in C₂HCl₅ reduction

Species	E ⁰ _{calc} (DFT-D)	E ⁰ _{calc} (CC)	E ⁰ _{exp}
{W ^{II} -O _{Me} }/ {W ^I -O _{Me} } ^{•-}	-2.45	-	-2,40
{W ^{III} -O _{Me} } ^{•+} / {W ^{II} -O _{Me} }	+0.68	-	+0.63
C₂HCl₅/C₂HCl₄[•] + Cl⁻	-0.66	-1.27 (-1.01)	(-0.98)
C ₂ HCl ₄ [•] /C ₂ HCl ₃ + Cl ⁻	+0.93	+0.80	
C ₂ HCl ₃ /cis-C ₂ HCl ₂ [•] + Cl ⁻	-1.66	-2.12 (-1.86)	(-1.86)
cis-C ₂ HCl ₂ [•] /cis-C ₂ HCl ₂ ⁻	-0.42	-0.48	
cis-C ₂ H ₂ Cl ₂ /cis-C ₂ H ₂ Cl [•] + Cl ⁻	-1.97	-2.36 (-2.10)	(-2.09)
cis-C ₂ H ₂ Cl [•] /C ₂ H ₂ + Cl ⁻	+0.99	+0.91 (+1.18)	
C ₂ Cl ₄ /C ₂ Cl ₄ ^{•-}	-2.32 (-2.14)	-2.66 (-2.48)	(-2.11)
C ₂ Cl ₄ /C ₂ Cl ₃ [•] + Cl ⁻	-1.57	-2.09 (-1.82)	(-1.73)
C ₂ Cl ₃ [•] /C ₂ Cl ₃ ⁻	-0.24	-0.24	
C ₂ HCl/C ₂ H [•] ...Cl ⁻	-2.12	-2.55 (-2.32)	
C ₂ HCl/C ₂ H [•] + Cl ⁻	-2.72	-2.94 (-2.68)	
C ₂ HCl/C ₂ H [•] + Cl ⁻	-2.72	-2.94 (-2.68)	

in V vs Fc, obtained in CH₂Cl₂ solvent (or DMF)

- Significant differences between DFT-D and CC results only in the case of dissociative reduction (due to errors in estimation of C-Cl bond strength in DFT)

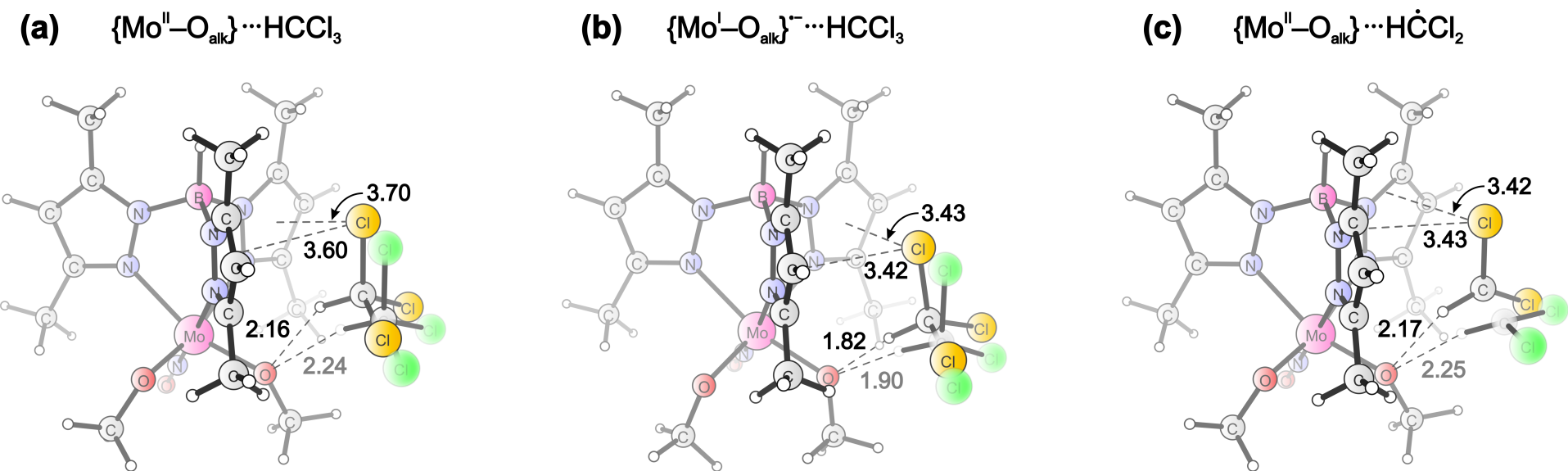
Inhibition of catalysis



DFT-D (COSMO/B3LYP-D3/def2-TZVPP) geometries of
(a) alcohol adduct, (b) alkene adduct

- Alcohols form stronger hydrogen bond than CHCl_3 and block the binding site
- Alkenes and DMF are bonded significantly weaker than CHCl_3
 - when added in great excess
 - inhibition occurs by trapping of transient $\text{CHCl}_2\bullet$ radical by alkene or $:\text{CCl}_2$ by DMF

Role of noncovalent interactions in electrocatalysis



Comparison of DFT-D (sharp, Cl atoms yellow) and DFT (diffused, Cl atoms green)

(a) $\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\} \cdots \text{HCCl}_3$, (b) $\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_3$, (c) $\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\} \cdots \text{HCCl}_2^{\bullet}$

- Significant differences in adducts geometries, especially in $\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_2^{\bullet}$, where hydrogen bond is weaker and has dispersive character
- Noncovalent interactions are crucial for stabilisation of adducts with weak hydrogen bond

Role of noncovalent interactions in electrocatalysis

Adduct	DFT	DFT//DFT-D3	DFT-D3 Opt
$\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\}^0 \cdots \text{HCCl}_3$	4.2	-32.2	-44.4
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_3$	-4.2	-42.7	-52.3
$\{\text{Mo}^{\text{II}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HCCl}_2^{\bullet}$	2.1	-23.8	-37.2
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HOCH}_3$	-22.2	-52.3	-56.1
$\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HC(=O)N(CH}_3)_2^{\text{a}}$	10.5	-22.6	-30.1
$\{\text{W}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{H}_2\text{C=CHCH}_3$	12.6	-11.3	-22.6

ΔG_{bind} in $\text{kJ}\cdot\text{mol}^{-1}$ in CH_2Cl_2 solvent (^a in DMF), BSSE corrected

- Noncovalent interactions are crucial for stabilisation of adducts with weak hydrogen bond
- Even $\{\text{Mo}^{\text{I}}-\text{O}_{\text{alk}}\}^{\bullet-} \cdots \text{HOCH}_3$ adduct with strong H-bond shows stabilisation effect from dispersive interactions
- Geometry optimization using DFT-D3 strongly recommended

Software remarks and computational details

- Gaussian03 and Gaussian09
 - used for DFT geometry optimizations and redox potentials calculations
 - wide spectrum of solvation methods
- Turbomole 6.x and 7.x
 - used for DFT-D3 geometry optimizations
 - very fast in geometry optimizations and BSSE estimations
 - only numerical frequencies calculations when COSMO model is used
 - embarrassingly parallel but consume big amount of resources (up to 120 cores for week)
- Molpro 2012 and 2015
 - used for parallel CCSD(T) calculations
 - can consume great amount of resources (up to 200 cores for weeks) due to scaling factor of $O(N^7)$

Outcome

- Rationalized mechanism of electrocatalytic dehalogenation of polychloroalkanes by Mo and W scorpionate alkoxides and its inhibition
 - combined action of C–H \cdots O_{alk} bonding and Cl \cdots π _{pyrazolyl} dispersive interactions may facilitate intramolecular electron transfer
- Shown that dispersion interactions could be crucial for stabilisation of weakly bonded adducts
 - DFT-D has to be used in such cases to yield reasonable results
- Established computational protocol for calculation of redox potentials for investigated Mo/W alkoxides and for organic chlorides with the accuracy of up to 0.05 V
- Computational resources have been provided by ACC Cyfronet AGH which is part of PLGrid Infrastructure

Publications

- P. P. Romańczyk, M. Radoń, K. Noga, S. S. Kurek, Autocatalytic cathodic dehalogenation triggered by dissociative electron transfer through a C–H···O hydrogen bond, *Phys. Chem. Chem. Phys.* 15 (2013) 17522.
- P. P. Romańczyk, K. Noga, M. Radoń, G. Rotko, S. S. Kurek, On the role of noncovalent interactions in electrocatalysis. Two cases of mediated reductive dehalogenation, *Electrochim. Acta*, 110 (2013) 619.
- P. P. Romańczyk, G. Rotko, K. Noga, M. Radoń, G. Andryianau, S. S. Kurek, The effect of C–H···O bonding and Cl··· π interactions in electrocatalytic dehalogenation of C2 chlorides containing an acidic hydrogen, *Electrochim. Acta* 140 (2014) 497.