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A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Biomimetic Thiyl Radical Formation from Diphenyl Disulfide with the Low Valent Ni(I) State of a Cofactor F430 Model

Samira Amini, Kerstin Oppelt, Olivier Blacque, Mikhail Agrachev, Gunnar Jeschke, and Felix Zelder*

Chem. Sci. **2025**.

<https://doi.org/10.1039/d4sc08416k>

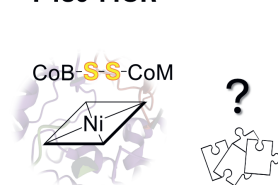
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Cofactor F430 is a nickel-containing hydrocorphinato complex with a key role in enzymatic methane formation and oxidation. F430-dependent methyl-coenzyme M reductase (MCR) catalyzes methane conversion in methanotrophic bacteria *via* a radical mechanism involving a transient thiyl radical. In this work, Amini and coworkers introduce a semi-artificial Ni-complex derived from vitamin B12 as a functional and structural model of F430. Electrochemical studies show that the Ni(I) complex facilitates the cleavage of diphenyl disulfide, generating approximately 0.5 equivalents of thiophenol and a transient thiophenyl radical. The reactive thiyl radicals can be trapped with phenylacetylene, yielding thiophenyl-substituted olefins, but also contribute to the degradation of the Ni-complex. This electrochemical model reaction replicates the initial step of the radical mechanism in anaerobic methane oxidation by MCR, offering new insights into F430-catalyzed processes.

Authors' comments:

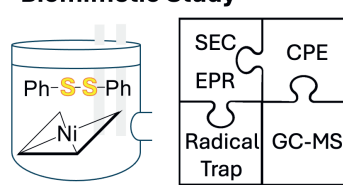
“We hope this research will help to unravel the mechanisms of methane production and oxidation by the enzyme methyl-coenzyme M reductase, paving the way for developing biomimetic catalysts for green energy applications. We thank our collaborators, whose insights and contributions made this journey both enriching and inspiring.”

F430-MCR



Mechanism of
S-S Cleavage

Biomimetic Study



Electrochemical cell
Mechanism of
S-S Cleavage

Ni-Catalyzed Enantioconvergent Kumada–Corriu Cross-Coupling between β -Bromostyrenes and Secondary Grignard Reagents: Reaction Development, Scope and Mechanistic Investigations

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ACS Catal. **2025**, *15*, 392.

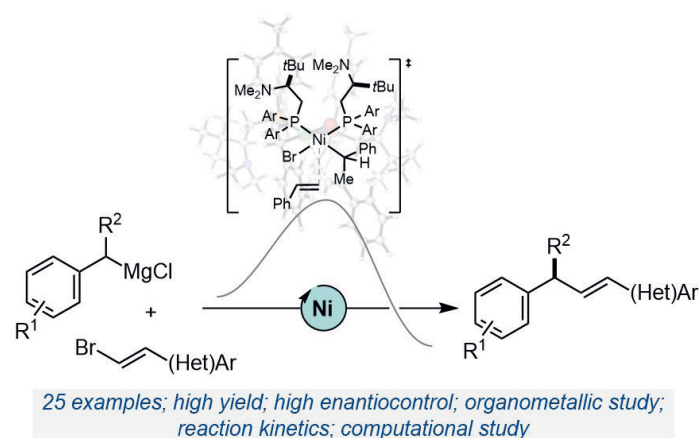
<https://doi.org/10.1021/acscatal.4c06360>

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A Ni-catalyzed enantioconvergent cross-coupling between β -bromostyrenes and secondary Grignard reagents is used for the C(sp²)–C(sp³) cross-coupling of a broad range of different products with good levels of enantio-induction. Mechanistic studies showed an unexpected binding mode of the chiral (P,N) ligand and support a radical rebound mechanism. Kinetic experiments identified an off-cycle resting state with dinuclear species. Computational analysis aligns with an Ni(I)/Ni(III) catalytic cycle and indicates that a radical capture event determines enantioselectivity, revealing insights into the dynamic kinetic resolution process, where the rapid epimerization of the secondary alkyl Grignard reagents occur *via* easily accessible trinuclear magnesium aggregates.

Authors' comments:

“There was much to learn by revisiting a reaction from the 80s. Despite a better mechanistic understanding, we believe there is still a lot to uncover about Ni-catalyzed cross-coupling reactions.”



Making Mo(0) a Competitive Alternative to Ir(III) in Phosphors and Photocatalysts

Tao Jin, Narayan Sinha, Dorothee S. Wagner, Alessandro Prescimone, Daniel Häussinger, and Oliver S. Wenger*

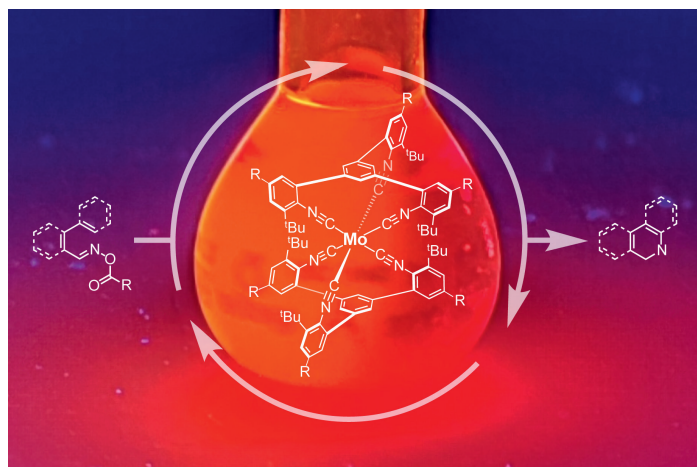
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<https://doi.org/10.1021/jacs.4c16672>

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Iridium-based complexes have been widely utilized in light-emitting devices and photocatalysis, but the scarcity of iridium has necessitated the development of alternatives based on more abundant metals. The use of first-row transition metals has generally resulted in poor luminescence and limited excited-state redox properties, making it difficult to match the performance of noble-metal-based photocatalysts. In this work, these challenges have been addressed through the use of a nonprecious second-row transition metal, molybdenum(0), with a tailored coordination sphere. Photoluminescence quantum yields comparable to those of iridium(III) complexes have been achieved, and photochemical reduction reactions that are not typically accessible with iridium-based systems have been enabled. These findings demonstrate that Earth-abundant metals can serve as viable alternatives in lighting technologies and metal-based photocatalysis. This approach provides a foundation for further exploration of non-noble metal complexes in advanced photochemical applications.

Authors' comments:

"Molybdenum is 1400 times more abundant than iridium. The ligands for the new molybdenum(0) complexes can be synthesized in just 5–6 straightforward steps, with simple purification processes involved."



Functionalized Terthiophene as an Ambipolar Redox System: Structure, Spectroscopy, and Switchable Proton-Coupled Electron Transfer

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The authors investigate an organic redox system capable of ambipolar electron transfer, a rare yet promising feature for applications in synthetic chemistry and energy science. In particular, the role of such systems in proton-coupled electron transfer (PCET) remains largely unexplored but could facilitate 'switchable' reactivity by regulating hydrogen atom exchange through redox control. This study reports the synthesis and characterization of a functionalized terthiophene (TTH) bearing methyl thioether and phosphine oxide groups, which exhibits reversible PCET behavior. Electrochemical analysis confirmed its capacity for oxidation and reduction, leading to the generation of cationic and anionic radicals. Structural, spectroscopic, and computational data revealed that these substituents modulate TTH's electronic properties, stabilizing both radical species. Upon oxidation, functionalized TTH acts as a hydrogen atom acceptor in PCET with 1,4-dihydroquinone, forming a hydroxyphosphonium species. This process reverses upon reduction, where functionalized TTH donates a hydrogen atom in PCET with 2,3-dimethylantraquinone. Thermochemical analysis demonstrated a 30 kcal/mol reduction in O–H bond strength, underpinning the system's switchable PCET activity. These findings establish a fundamental framework for leveraging ambipolarity in organic redox chemistry to modulate PCET processes.

Authors' comments:

"Proton-coupled electron transfer (PCET) is central to energy storage and synthesis, yet typically involves transition metals. Our work demonstrates that PCET can be controlled in an all organic system using a redox stimulus as a 'switch'."

