Coordination Chemistry

DOI: 10.1002/anie.201204100

Redox-Active Ligands in Catalysis

*Vijayendran K. K. Praneeth, Mark R. Ringenberg, and Thomas R. Ward**

base metals · biomimetic catalysis · homogeneous catalysis · multi-electron transformations · redox-active ligands

Dedicated to Roald Hoffmann on the occasion of his 75th birthday

Nature's use of redox-active moieties combined with 3d transition-metal ions is a powerful strategy to promote multi-electron catalytic reactions. The ability of these moieties to store redox equivalents aids metalloenzymes in promoting multi-electron reactions, avoiding high-energy intermediates. In a biomimetic spirit, chemists have recently developed approaches relying on redox-active moieties in the vicinity of metal centers to catalyze challenging transformations. This approach enables chemists to impart noble-metal character to less toxic, and cost effective 3d transitional metals, such as Fe or Cu, in multi-electron catalytic reactions.

> *"Formalisms are convenient fictions which contain a piece of the truth"*
> Roald Hoffmann[1]

1. Introduction

To avoid high activation barriers, nature typically breaks down challenging catalytic transformations into a sequence of elementary steps. This strategy is particularly versatile in the context of sustainable energy whereby energetically costly multi-electron processes are required to transform stable molecules (e.g. N_2, H_2O, CO_2, CH_4) into energy-rich fossil-fuel surrogates. To address this challenge in redox catalysis, nature has developed enzymes that distribute redox equivalents over several atoms, for example, metal clusters, redox-active ligands, and amino acids.[2] This approach allows enzymes to operate very close to the thermodynamic potential dictated by the reaction (Figure 1).

Redox-active ligands often facilitate vital multi-electron catalytic transformations.[3] Nature relies on redox-active moieties, either bound as ligands or in the second coordination sphere of a metal cofactor, to catalyze challenging reactions. The prosthetic groups involved in redox reactions may contain the following features: 1) a "non-innocent" redox-neutral ligand, 2) a redox-active ligand, and/or 3) a redox-active moiety within the metal's second coordination sphere (Scheme 1).

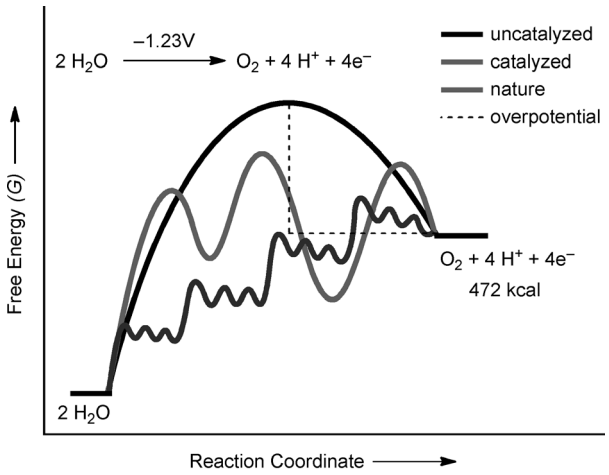
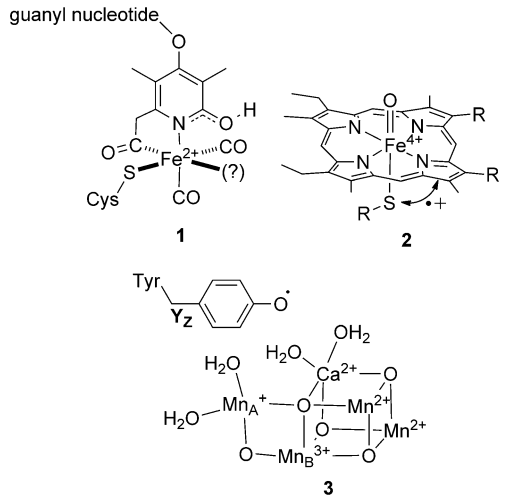


Figure 1. Breaking down a multi-electron redox reaction into distinct steps allows nature to circumvent high kinetic barriers.

The most recent addition to the hydrogenase family is the iron-only hydrogenase (Hmd) **2** that contains a bidentate 2-pyridone ligand.[4] Importantly, the iron remains in its Fe^{II} state throughout the processing of dihydrogen. This is made possible thanks to the presence of a non-innocent but formally redox-neutral ligand, which can exist as two tautomeric forms: 2-pyridone and 2-hydroxypyridine.

The electronic structure of cytochrome P450, responsible for the oxidation of unactivated C–H bonds, can be regarded as an iron(V)oxo species; however, the current description is a Fe^{IV}(O)porphyrin($^{\bullet+}$) (**1**).[5] Cytochrome P450 tames the

[*] Dr. V. K. K. Praneeth, Dr. M. R. Ringenberg, Prof. T. R. Ward
Department of Chemistry, University of Basel
Spitalstrasse 51, 4056 Basel (Switzerland)
E-mail: thomas.ward@unibas.ch



Scheme 1. Selected redox-active prosthetic groups that catalyze multi-electron transformations. Active site structure of [Fe]-hydrogenase **1** involved in the direct H_2-transfer, key oxo-ferryl intermediate **2** of cytochrome P450 for the two-electron oxidation of organic substrates, and structure of the oxygen-evolving complex **3** including a second-coordination-sphere tyrosine residue involved in the multi-electron water-splitting reaction in photosystem II.

reactivity by distributing one oxidizing equivalent over the porphyrin and proximal cysteine ligand.[6]

Concerning second coordination sphere redox-active moieties within metalloenzymes, tyrosine residues and Fe–S clusters occupy a place of choice.[7] In the oxygen evolving complex (OEC), the tyrosine residue (Y_z) is optimally positioned in the second coordination sphere to orchestrate the sequential proton and electron trafficking between the primary donor of photosystem II (P680) and the OEC **3**.[8] Such subtle position optimization is also found with Fe–S clusters, in which electron-transfer enzymes are finely tuned compared to synthetic Fe–S models.[9]

The multi-electron processes found throughout nature utilize metals that are dominated by single electron redox events (e.g. Fe, Mn, Cu). Homogeneous catalysis is, however, dominated by noble metals, such as Pd or Rh, which readily undergo two-electron processes. Nature uses redox-active moieties to store and mediate electron-transfer to metal centers thereby imparting noble metal character onto base metals. In this Minireview, we outline recent biologically inspired efforts to exploit redox-active ligands in catalysis.

2. Non-Innocent Ligands

As illustrated by Hmd, formally redox-neutral but "non-innocent" ligands may exist in two tautomeric forms varying between an anionic and a neutral donor ligand. Even before the discovery of Hmd, several non-innocent ligands were successfully exploited in catalysis.[10] The widely acclaimed Shvo's ruthenium catalyst[11] and Knölker's iron analogue **4**[12] are reminiscent of the Hmd active site.[13] The iron complex **4** is attracting increasing attention as hydrogenation catalyst owing to the use of inexpensive and non-toxic iron.[14] The two representations of complex **4** (Scheme 2) highlight the ambiguity in assigning the formal oxidation state of the metal and thus suggest that such ligands indeed act as electron reservoir.

Along similar lines, Milstein and co-workers have exploited several pincer ligands with "pyridone-like" character to catalyze various challenging reactions.[15] Most notably, the ruthenium complex **5** is capable of sequential water splitting (Scheme 3). The splitting of water is afforded by the dearomatized ruthenium complex **5** that initially reacts with water to yield the hydrido–hydroxo complex **6**. Complex **6** subsequently reacts with water at 100 °C to liberate H_2, yielding the bis(hydroxo) complex, **7**. Upon photolysis, dioxygen is released, regenerating the hydride **6**.[16] This reaction sequence, formally water splitting, constitutes a unique approach towards developing new catalysts based on non-innocent ligands.

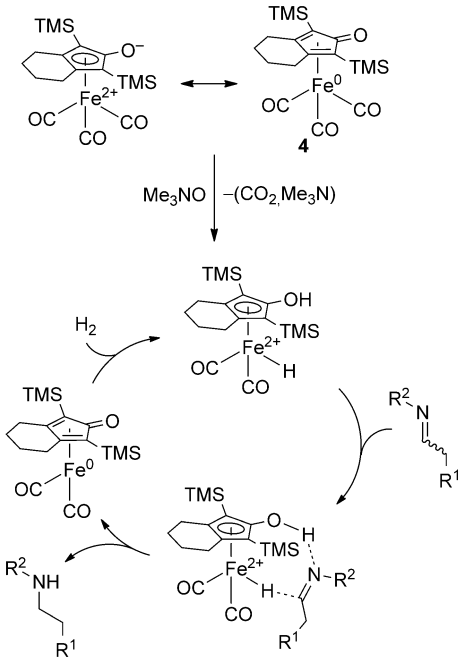
3. Redox Active Ligands

The use of precious metals in homogeneous catalysis has been ubiquitous for the last 200 years for nearly all two-

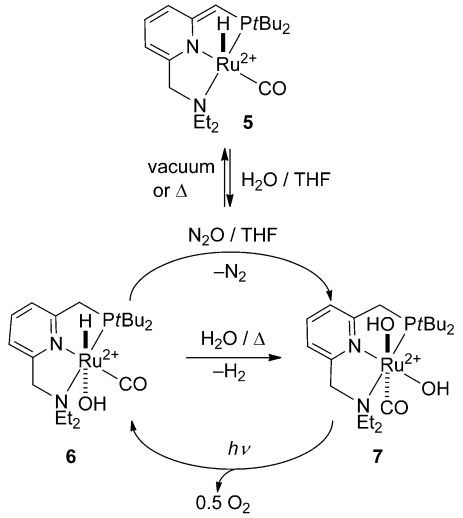
V. K. K. Praneeth obtained his Ph.D. in Inorganic Chemistry in 2008 from the University of Kiel (Germany) and the University of Michigan (USA) under the guidance of Prof. Nicolai Lehnert. Then he moved to the University of Minnesota (USA) as postdoctoral fellow under the guidance of Prof. Lawrence Que, working on nonheme iron-catalyzed cis-dihydroxylation chemistry. At present, he is in the Ward group as a post-doctoral researcher looking at various oxidation reactions based on artificial metalloenzymes using non-innocent ligands.

Mark Ringenberg received Ph.D. in Inorganic Chemistry in 2011 at the University of Illinois at Urbana under the guidance of Thomas B. Rauchfuss working on redox active ligands in catalysis. He is currently a post-doctoral researcher at the University of Basel. His research concerns the interface of transition-metal catalysts and biology to generate artificial metalloenzymes for the processing of small molecules.

Thomas Ward obtained his Ph.D. under Prof. L. M. Venanzi from ETH Zurich in 1991. Following two postdocs (Profs R. Hoffmann, Cornell and C. Floriani, Lausanne), he initiated his independent career in bioinorganic chemistry at the University of Berne before moving to the University of Neuchâtel in 2000. In 2008, he moved to the University of Basel. In a biomimetic spirit, his research is centered on the exploitation of second coordination sphere interactions in catalysis.

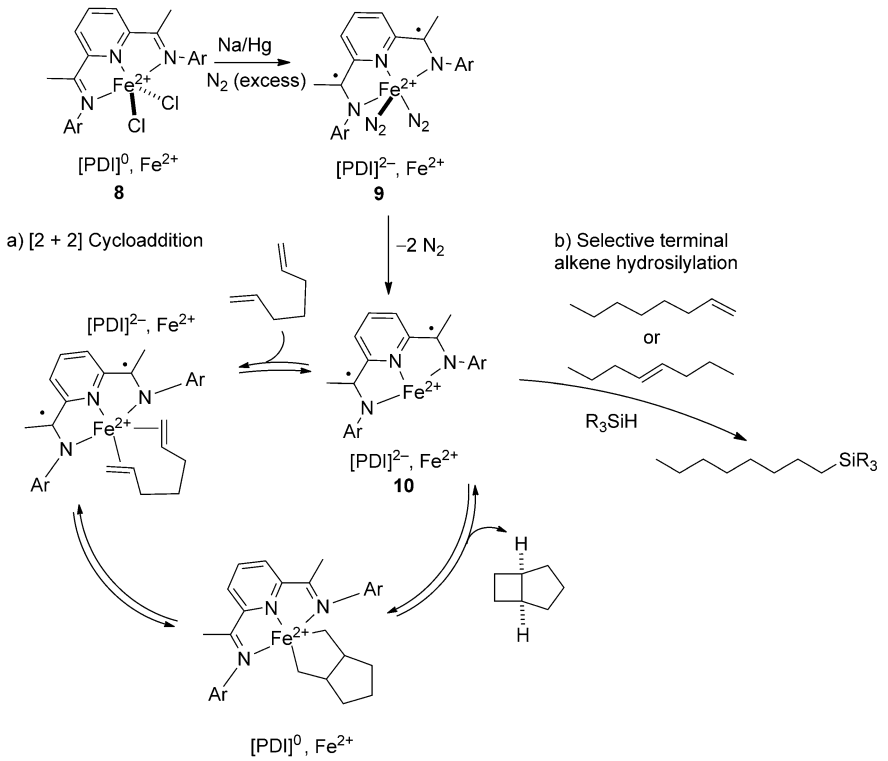


Scheme 2. Reductive amination of aliphatic aldehydes and imines using Knölker's catalyst **4**.



Scheme 3. Milstein's ruthenium-catalyzed thermal dihydrogen and light-induced dioxygen evolution from water.

electron transformations. Drawing inspiration from nature, the development of catalysts based on abundant base metals has grown to address the environmental, health, and financial issues associated with precious metals. Chirik and co-workers have developed several iron and cobalt catalysts that elicit multi-electron redox chemistry assisted by the presence of a redox-active ligand, based on bis(imino)pyridine (PDI; Scheme 4).[17] The bis(imino)pyridine ligands have four accessible oxidation states and participate in redox reactions which enables the metal to mediate multiple electron processes.[3d] The iron(II) complex [Fe(PDI)Cl_2] (**8**) is reduced under dinitrogen with sodium amalgam to afford the bis(dinitrogen) precatalyst, **9**. The electronic structure of



Scheme 4. Versatile organic transformations catalyzed by $[Fe^{II}(PDI)]^{2-}$: a) [2+2] cycloaddition reaction and b) olefin isomerization and hydrosilylation of unfunctionalized alkenes.

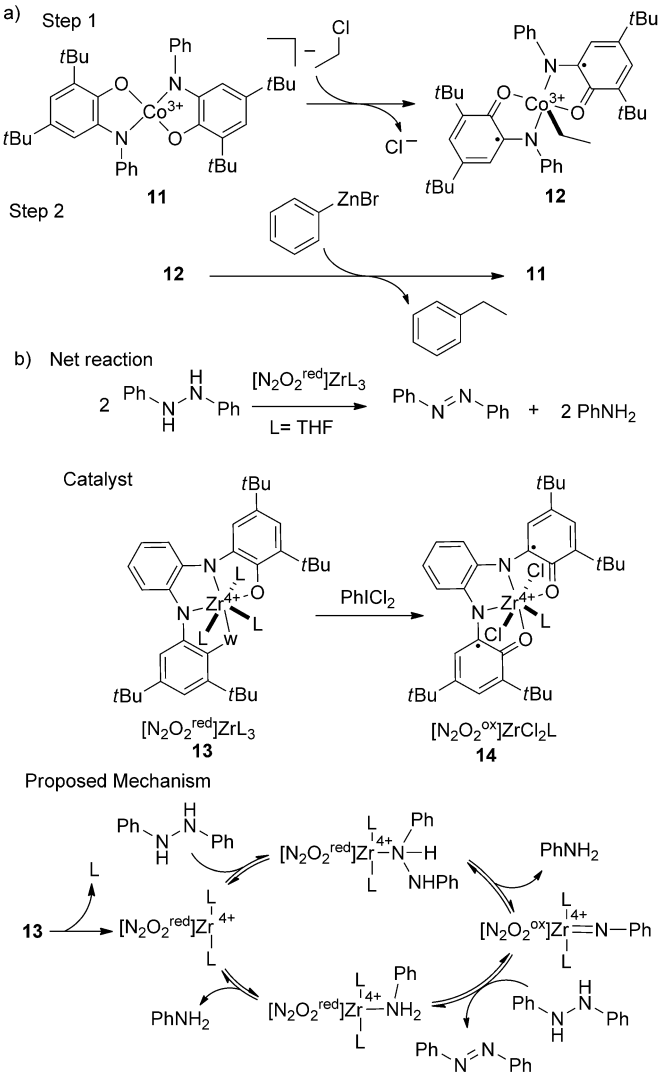
this pre-catalyst has been thoroughly characterized by spectroscopic techniques (NMR, X-ray absorption (XAS), X-ray emission (XES), and Mössbauer) combined with density functional theory (DFT) calculations. The two-electron reduction is localized on the PDI ligand rather than on the metal center.[18] This feature is thought to be critical for the iron-catalyzed [2+2] cycloaddition reaction of dienes to afford the corresponding bicyclo-[3,2,0]-heptane (Scheme 4a). The reaction does not proceed in the presence of redox inactive ligands, for example, a pyridine bis(carbene) ligand.[18a] More recently, the reduced bis(imino)pyridine iron complex **10** was used as a hydrosilylation catalyst for unactivated olefins with tertiary silanes (Scheme 4b). The catalyst **10** also induces an internal olefin to chain walk to the terminal position prior to hydrosilylation.[19]

Since 2000, bulky amidophenolate ligands (ap^{2-}), popularized by the work of Wieghardt, have been widely exploited as redox-active ligands in which much of the electron trafficking occurs on the ligand rather than on the metal.[20]

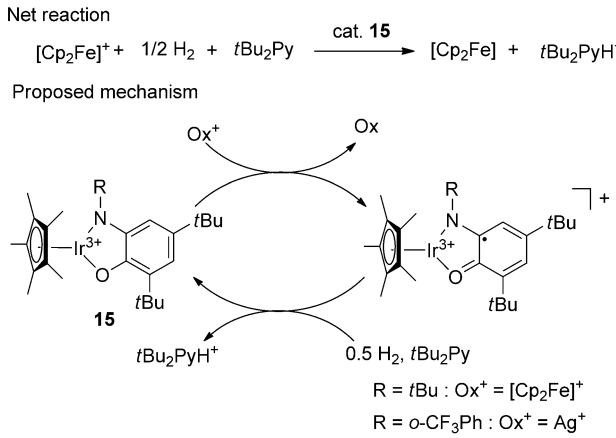
Soper and co-workers developed a $[Co(ap)_2]^-$ (**11**) system for Negishi-type C–C cross-coupling reactions. In the presence of alkyl halides, the complex undergoes formal oxidative addition, leading to the formation of a Co–C bond. The metal center maintains its formal 3+ oxidation state with an intermediate spin with each aminophenolate providing one electron to afford the corresponding [Co^{III}(iminosemiquinone)$_2$(CH_2CH_3)] (**12**).[21] The metal formally maintains the same oxidation state in both oxidative addition and reductive elimination steps. Subsequent treatment of **12** with an organozinc compound leads to the cross-coupling product, reminiscent of a reductive elimination step (Scheme 5a); however, this reaction is not yet catalytic. Related work by Heyduk and co-workers combined amido bis(phenolate) ligands with Zr^{IV}, in compound **13**, to afford formal oxidative addition to give **14**, and reductive elimination from a d^0 metal (Scheme 5b).[22] Recently **13** was used to achieve catalytic turnover for the disproportionation of 1,2-diphenyl hydrazine to the corresponding aniline and azobenzene (Scheme 5b).[23] Such systems resemble the zinc-containing alcohol dehydrogenases; the redox-neutral metal center binds, positions, and activates the substrate but the redox event exclusively occurs on the NAD^+/NADH couple.[24]

Dihydrogen oxidation was achieved by Rauchfuss and co-workers upon combining an ap^{2-} ligand with a [Cp*Ir^{III}] moiety in **15** (Cp* = η-C_5Me_5).[25] Whereas the fully reduced piano-stool complex is unreactive towards Lewis bases, upon one-electron oxidation, the metal becomes Lewis acidic and binds Lewis bases, for example, CN^-, PR_3, and CH_3CN. In the presence of a non-coordinating base, dihydrogen reacts to reduce the iminosemiquinone ($ap^{\bullet-}$) to amidophenolate (ap^{2-}), releasing a proton. Catalytic turnover was achieved by combining an oxidizing agent (ox^+), Ag^+ or $[Cp_2Fe]^+$ (Cp = η-C_5H_5), a base, and dihydrogen (Scheme 6). Complex **15** acts as a dihydrogen oxidation catalyst, a critical step in both hydrogenase functionality and the cathodic side of a hydrogen fuel cell.

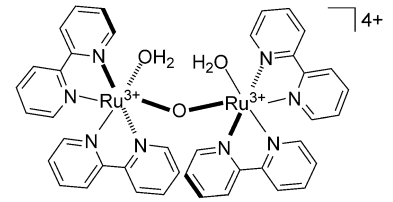
Inspired by Meyer's remarkable ruthenium blue dimer **16** that catalyzes the oxidation of water,[26] Tanaka and co-workers demonstrated the electrochemical oxidation of water



Scheme 5. Redox-active amidophenolate-type ligands critically involved in a) a carbon–carbon formation reaction and b) the catalytic disproportionation diphenylhydrazine.

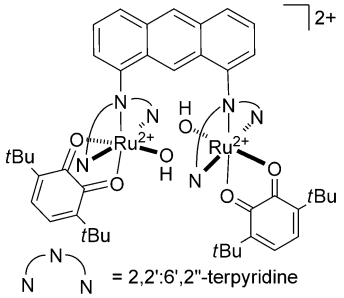


Scheme 6. The catalytic oxidation of dihydrogen using [Cp*Ir(ap)] as the catalyst.



redox: $Ru^{3+}/Ru^{4+}Ru^{5+}$

16



redox: Ru^{2+}/Ru^{3+} coupled with quinone/semiquinone

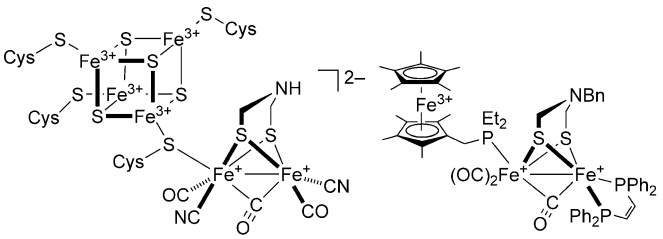
17

Scheme 7. Diruthenium catalysts for water oxidation: Meyer's original ruthenium blue dimer **16** and Tanaka's system bearing quinone moieties **17**. The blue dimer is proposed to involve high-valent Ru intermediates (Ru^{IV} and/or Ru^{V}) at each Ru center in the catalytic cycle.[29] In contrast, Tanaka's system involves redox changes at the quinone moiety combined with a Ru^{II}/Ru^{III} couple.

using a ruthenium catalyst containing a *o*-quinone ligand **17** (Scheme 7).[27] Quinone can adopt three different oxidation states: quinone, semiquinone, and catecholate. The resulting dinuclear complex displays remarkable water oxidation activity with high turnover numbers (TON > 30000). Unlike other water-oxidation catalysts, which rely on high valent ruthenium oxo species, Tanaka's system shuttles between Ru^{II} and Ru^{III}, coupled with ligand-centered (i.e. semiquinone/quinone) redox couples.[28]

4. Redox-Active Moieties in the Second Coordination Sphere of a Metal

The presence of a redox-active $[Fe_4S_4]$ iron cluster in the vicinity of the di-iron moiety is considered to be one of the key factors responsible for the low over-potential and exceptional performance of the [FeFe]-hydrogenases (**18**; Scheme 8).[30] The importance of the redox-active moiety in the second coordination sphere of the [FeFe]-hydrogenase's active site was recently highlighted by Rauchfuss and co-workers.[31] They demonstrated that both a redox-active ferrocenyl phosphine moiety and a pendant amine on the bridging ligand in catalyst **19** were critical to the oxidation of dihydrogen at low pressure and room temperature. Hydrogen oxidation is exothermic and displays a large kinetic barrier at room temperature; nature overcomes this by rapidly separating the electron from the proton through the redox-active second coordination sphere moiety and a pendant amine.[31]



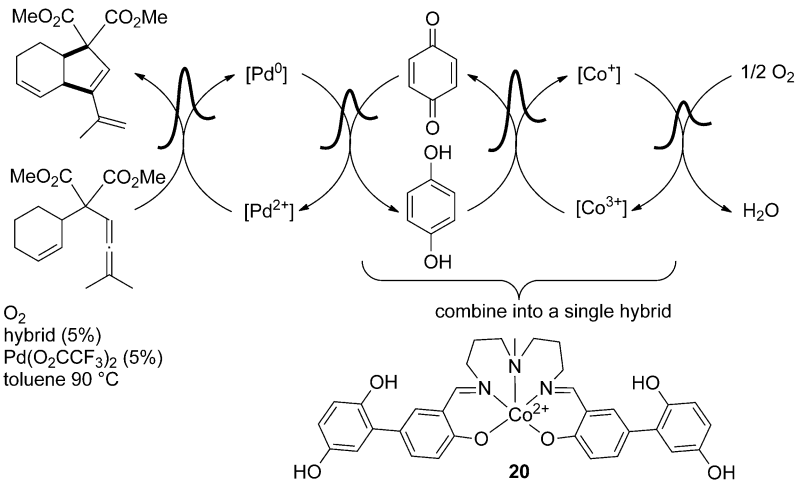
18 **19**

Scheme 8. Structure of the active site of the [FeFe]-hydrogenase enzyme **18** and Rauchfuss' model **19**. The enzyme mimic requires both the redox-active ferrocenium second coordination sphere moiety and the non-innocent aza strap to achieve catalytic efficiency.

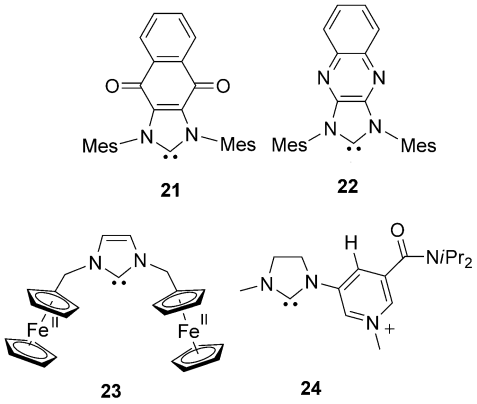
Nature often relies on quinone cofactors as mobile two-electron transfer mediators (ETM). In homogeneous catalysis, quinones have been used as efficient ETMs to facilitate Pd^{II} regeneration by air in Wacker-type oxidative transformations.[32] This reoxidation process mediated by a quinone inhibits palladium black formation. In a biomimetic spirit, adding additional ETMs with an appropriate redox potential between the terminal oxidant and the catalyst allows the activation energy to be further lowered thus enabling to catalysis to be performed near the thermodynamic potential. Bäckvall and co-workers have mastered this strategy by combining an O_2-activating metal complex, for example, phtalocyanines or a Schiff-base ligand metal complex, a quinone moiety, and a metal catalyst that binds and oxidizes the substrate. These elegant redox cascade reactions mimic some of nature's low-energy pathways, such as those found in the respiratory chain. Covalently linking the hydroquinone, **20** with the metal complex further contributes to lowering the activation energy of the oxidation process, thereby highlighting the importance of a suitably positioned second coordination sphere redox-active moiety in catalysis (Scheme 9).[33]

N-heterocyclic carbene ligands (NHC) are renowned for the strength of their M–C interaction, irrespective of the oxidation state of the metal center.[34] Adding a redox-active moiety to a NHC gives interesting properties to the resulting metal complexes. In this context, NHCs bearing a naphthoquinone **21**,[35] a quinoxaline **22**,[36] a ferrocene **23**,[37] or a nicotinamide **24**[38] moiety have recently been reported (Scheme 10). The oxidation state of the redox-active NHC-ligand **21** was shown to play a critical role in the nickel(II)-catalyzed Kumada cross-coupling between PhMgCl and bromoarenes.[35] Catalysis can be reversibly arrested and subsequently restored by addition of cobaltocene or ferrocenium, respectively. This remarkable behavior is attributed to redox changes at the quinone moiety rather than at the metal.

Introducing an active hydrogen-atom transfer moiety into the second coordination sphere of a metal center, as found in **20**–**22**, may allow proton-coupled electron-transfer processes to be catalyzed, thus avoiding the formation of high-energy intermediates.[39] This attractive feature may prove vital to address some of the current grand challenges facing the



Scheme 9. Bäckvall's hybrid hydroquinone/cobalt Schiff-base (**20**) as an efficient hybrid mediator for palladium-catalyzed aerobic oxidative coupling reactions. Each redox step displays a low activation energy thus resulting in an efficient overall catalytic transformation (See Figure 1).



Scheme 10. N-heterocyclic carbene ligands containing redox-active moiety.

catalysis community, such as C–H bond oxidation, H_2 oxidation, water oxidation, carbon dioxide reduction, and dinitrogen reduction.

5. Outlook

Recent progress in catalysis using redox-active ligands is highlighted in this Minireview. While the use of non-innocent ligands is well documented in catalysis, redox-active ligands represent a much younger addition to the metal-catalysis repertoire. Unfortunately, some of the most interesting examples of catalytic transformations using redox-active ligands still rely on precious metals. A major effort in the area of base-metal coordination chemistry and catalysis is indispensable. Mimicking the function of metalloenzymes can lead to the use of more environmentally friendly non-precious metals instead of the currently used noble metals. For a deeper understanding of the fine electronic balance between the metal center and ligand, which is responsible for the catalytic properties of the metal complex, further studies on reactivity in combination with spectroscopic investigations are required.

T.R.W. thanks the Swiss National Science Foundation for generous support (Grant 200021_140242).

Received: May 26, 2012
Published online: September 20, 2012

[1] J. Y. Saillard, R. Hoffmann, *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.
[2] M. Rakowski DuBois, D. L. DuBois, *Acc. Chem. Res.* **2009**, *42*, 1974–1982.
[3] a) W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **1987**, *76*, 187–235; b) W. Kaim, *Inorg. Chem.* **2011**, *50*, 9752–9765; c) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270–279; d) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794–795.
[4] a) O. Pilak, B. Mamat, S. Vogt, C. H. Hagemeier, R. K. Thauer, S. Shima, C. Vonrhein, E. Warkentin, U. Ermler, *J. Mol. Biol.* **2006**, *358*, 798–809; b) S. Shima, E. J. Lyon, M. Sordel-Klippert, M. Kauss, J. Kahnt, R. K. Thauer, K. Steinbach, X. Xie, L. Verdier, C. Griesinger, *Angew. Chem.* **2004**, *116*, 2601–2605; *Angew. Chem. Int. Ed.* **2004**, *43*, 2547–2551; c) M. T. Stiebritz, M. Reiher, *Inorg. Chem.* **2010**, *49*, 5818–5823.
[5] J. Rittle, M. T. Green, *Science* **2010**, *330*, 933–937.
[6] P. R. Ortiz de Montellano, *Chem. Rev.* **2010**, *110*, 932–948.
[7] M. Cordes, B. Giese, *Chem. Soc. Rev.* **2009**, *38*, 892–901.
[8] a) C. W. Hoganson, G. T. Babcock, *Science* **1997**, *277*, 1953–1956; b) A. M. Hays, I. R. Vassiliev, J. H. Golbeck, R. J. Debus, *Biochemistry* **1999**, *38*, 11851–11865; c) Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55–U65.
[9] a) T. A. Rouault, W.-H. Tong, *Nat. Rev. Mol. Cell Biol.* **2005**, *6*, 345–351; b) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, J. F. Weiher, *Proc. Natl. Acad. Sci. USA* **1972**, *69*, 2437–2441.
[10] a) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308; b) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393–406.
[11] a) Y. Shvo, D. Czarkie, Y. Rahamim, D. F. Chodosh, *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402; b) B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev.* **2010**, *110*, 2294–2312.

[12] a) H. J. Knölker, E. Baum, H. Goesmann, R. Klauss, *Angew. Chem.* **1999**, *111*, 2196 – 2199; *Angew. Chem. Int. Ed.* **1999**, *38*, 2064 – 2066; b) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2007**, *129*, 5816 – 5817.

[13] a) P. J. Turrell, J. A. Wright, J. N. T. Peck, V. S. Oganesyan, C. J. Pickett, *Angew. Chem.* **2010**, *122*, 7670 – 7673; *Angew. Chem. Int. Ed.* **2010**, *49*, 7508 – 7511; b) D. F. Chen, R. Scopelliti, X. L. Hu, *Angew. Chem.* **2011**, *123*, 5789 – 5791; *Angew. Chem. Int. Ed.* **2011**, *50*, 5671 – 5673.

[14] a) C. Sui-Seng, F. Freutel, A. J. Lough, R. H. Morris, *Angew. Chem.* **2008**, *120*, 954 – 957; *Angew. Chem. Int. Ed.* **2008**, *47*, 940 – 943; b) A. Pagnoux-Ozherelyeva, N. Pannetier, M. D. Mbaye, S. Gaillard, J. L. Renaud, *Angew. Chem.* **2012**, *124*, 5060 – 5064; *Angew. Chem. Int. Ed.* **2012**, *51*, 4976 – 4980.

[15] a) R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 10122 – 10126; *Angew. Chem. Int. Ed.* **2011**, *50*, 9948 – 9952; b) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 2168 – 2172; *Angew. Chem. Int. Ed.* **2011**, *50*, 2120 – 2124; c) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588 – 602.

[16] S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74 – 77.

[17] a) S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794 – 13807; b) M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13340 – 13341; c) K. T. Sylvester, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8772 – 8774.

[18] a) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13901 – 13912; b) Q. Knijnenburg, S. Gambarotta, P. H. Budzelaar, *Dalton Trans.* **2006**, 5442 – 5448.

[19] A. M. Tondreau, C. C. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. Delis, P. J. Chirik, *Science* **2012**, *335*, 567 – 570.

[20] a) P. Chaudhuri, K. Wieghardt, T. Weyhermüller, T. K. Paine, S. Mukherjee, C. Mukherjee, *Biol. Chem.* **2005**, *386*, 1023 – 1033; b) H. Chun, T. Weyhermüller, E. Bill, K. Wieghardt, *Angew. Chem.* **2001**, *113*, 2552 – 2555; *Angew. Chem. Int. Ed.* **2001**, *40*, 2489 – 2492; c) P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 2213 – 2223; d) C. Nazari Verani, S. Gallert, E. Bill, T. Weyhermüller, K. Wieghardt, P. Chaudhuri, *Chem. Commun.* **1999**, 1747 – 1748.

[21] A. L. Smith, K. I. Hardcastle, J. D. Soper, *J. Am. Chem. Soc.* **2010**, *132*, 14358 – 14360.

[22] a) K. J. Blackmore, J. W. Ziller, A. F. Heyduk, *Inorg. Chem.* **2005**, *44*, 5559 – 5561; b) N. A. Ketterer, H. Fan, K. J. Blackmore, X. Yang, J. W. Ziller, M.-H. Baik, A. F. Heyduk, *J. Am. Chem. Soc.* **2008**, *130*, 4364 – 4374.

[23] K. J. Blackmore, N. Lal, J. W. Ziller, A. F. Heyduk, *J. Am. Chem. Soc.* **2008**, *130*, 2728 – 2729.

[24] J. F. Biellmann, *Acc. Chem. Res.* **1986**, *19*, 321 – 328.

[25] M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788 – 789.

[26] J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, T. J. Meyer, *Acc. Chem. Res.* **2009**, *42*, 1954 – 1965.

[27] a) T. Wada, K. Tsuge, K. Tanaka, *Angew. Chem.* **2000**, *112*, 1539 – 1542; *Angew. Chem. Int. Ed.* **2000**, *39*, 1479 – 1482; b) T. Wada, K. Tsuge, K. Tanaka, *Inorg. Chem.* **2001**, *40*, 329 – 337; c) J. T. Muckerman, D. E. Polyansky, T. Wada, K. Tanaka, E. Fujita, *Inorg. Chem.* **2008**, *47*, 1787 – 1802; d) M. K. Tsai, J. Rochford, D. E. Polyansky, T. Wada, K. Tanaka, E. Fujita, J. T. Muckerman, *Inorg. Chem.* **2009**, *48*, 4372 – 4383.

[28] a) S. Ghosh, M.-H. Baik, *Angew. Chem.* **2012**, *124*, 1247 – 1250; *Angew. Chem. Int. Ed.* **2012**, *51*, 1221 – 1224; b) S. Ghosh, M.-H. Baik, *Inorg. Chem.* **2011**, *50*, 5946 – 5957.

[29] a) X. Yang, M.-H. Baik, *J. Am. Chem. Soc.* **2006**, *128*, 7476 – 7485; b) J. K. Hurst, J. Zhou, Y. Lei, *Inorg. Chem.* **1992**, *31*, 1010 – 1017.

[30] a) A. J. Pierik, M. Hulstein, W. R. Hagen, S. P. J. Albracht, *Eur. J. Biochem.* **1998**, *258*, 572 – 578; b) A. S. Pandey, T. V. Harris, L. J. Giles, J. W. Peters, R. K. Szilagyi, *J. Am. Chem. Soc.* **2008**, *130*, 4533 – 4540.

[31] J. M. Camara, T. B. Rauchfuss, *Nat. Chem.* **2012**, *4*, 26 – 30.

[32] J. Piera, J. E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558 – 3576; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506 – 3523.

[33] B. W. Purse, L. H. Tran, J. Piera, B. Åkermark, J.-E. Bäckvall, *Chem. Eur. J.* **2008**, *14*, 7500 – 7503.

[34] a) T. Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094 – 7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940 – 6952; b) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. Ceasar, *Chem. Rev.* **2011**, *111*, 2705 – 2733.

[35] A. G. Tennyson, V. M. Lynch, C. W. Bielawski, *J. Am. Chem. Soc.* **2010**, *132*, 9420 – 9429.

[36] S. Saravanakumar, M. K. Kindermann, J. Heinicke, M. Kockerling, *Chem. Commun.* **2006**, 640 – 642.

[37] C. D. Varnado, Jr., V. M. Lynch, C. W. Bielawski, *Dalton Trans.* **2009**, 7253 – 7261.

[38] a) A. McSkimming, M. Bhadbhade, S. B. Colbran, *Dalton Trans.* **2010**, *39*, 10581 – 10584; b) A. McSkimming, G. E. Ball, M. M. Bhadbhade, S. B. Colbran, *Inorg. Chem.* **2012**, *51*, 2191 – 2203.

[39] J. J. Warren, T. A. Tronic, J. M. Mayer, *Chem. Rev.* **2010**, *110*, 6961 – 7001.