Cooperative Catalysis with First-Row Late Transition Metals

Jarl Ivar van der Vlugt*[a]

Cooperative catalysis with first-row transition metals holds much promise for future developments regarding sustainable, selective transformations, including e.g. alkenes, dienes and a variety of small molecules such as CO_2, N_2 and water. This non-exhaustive analysis of the current state-of-the-art aims to give a comprehensive overview of the various design strategies and applications of first-row transition metal cooperative reactivity and to provide leads for new research initiatives in order to expand this emerging field. The main aspects covered involve bimetallic cooperativity, redox-noninnocent ligands in combination with first-row transition metal complexes, otherwise reactive or noninnocent scaffolds that can induce metal-ligand bifunctional substrate activation and the design of adaptive ligands and complexes thereof, wherein hemilability is a key factor for selective reactivity. The metals under review are primarily the late transition metals Fe, Co, Ni and Cu.

1. Introduction

Many elements from the Periodic Table are available in very limited supply, whilst resources are increasingly depleted as a result of the ever-growing global population, the rising average level of welfare and related demands for energy and chemical products. Catalysis is *the* key technology for the efficient conversion of raw materials into valuable products, but many catalysts themselves are based on scarce, expensive and noble materials such as second- and third-row transition metals. This is not sustainable for the future application of catalysts and new approaches and concepts need to be developed.

Nature has perfected the application of cheap, earth-abundant first-row transition metals for the execution of noble tasks such as small molecule activation or the functionalization and selective conversion of challenging substrates.[1] However, the (metallo)enzyme active sites employed very often rely on the reactivity of neighbouring ligand scaffolds and second coordination sphere interactions,

i.e. Nature makes use of *cooperative catalysis* and "bifunctional activation" is an ubiquitous concept in the chemistry of biological systems.[2] This principle covers many seemingly unrelated types of functionalities wherein the protein scaffold or co-factors around the active site actively facilitate substrate turnover in a way that would not be possible or not as efficiently achieved without the element of cooperativity.

The mode of action of e.g. the enzymes galactose oxidase[3] and the hydrogenases[4] are based (in part) on cooperative effects induced by the ligand sphere around the metal active site. Similar arguments can be used to qualify the bi- or oligonuclear nature of many active sites to steer and control substrate activation and functionalization processes, often also involving multi-electron redox events as well as proton-coupled electron-transfer phenomena. Many metalloenzymes utilize such multimetallic cooperative systems for selective transformations, including copper-based oxidases and oxygenases,[5] non-heme iron-based active sites,[6,7] dinuclear nickel-containing systems[8] as well as many mixed-metal biocatalysts.[9] The use of "flexidentate" or hemilabile ligation[10] can also be included as a commonly observed strategy to regulate accessibility to the active site and thereby control reactivity.

[a] Supramolecular & Homogeneous Catalysis, van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands Fax: +31-20-5255604 E-mail: j.i.vandervlugt@uva.nl

Jarl Ivar van der Vlugt (1975) earned his PhD with Prof. Vogt at the Eindhoven University of Technology (TUle) in 2003, working on ligand design and homogeneous catalysis, for which he received the 2004 KNCV Catalysis prize. After postdoctoral research with prof. Rauchfuss (UIUC) and with Prof. Meyer (Göttingen), as an Alexander-von-Humboldt Fellow, he obtained an NWO-CW VENI Grant to start his independent career at the TUle in 2007. Late 2008 he became assistant professor at the van't Hoff Institute for Molecular Sciences at the University of Amsterdam (UvA). His scientific interests are in small molecule activation, hydroamination, CO_2 functionalization, catalysis for green energy applications, (bimetallic) cooperative catalysis and ligand design. He was recently awarded an ERC Starting Grant to expand his research in the area of cooperative first-row transition metal catalysis.

In contrast to the many very successful examples of cooperative catalysis based on abundant metals for selective transformations in biological systems,[13] the design and utilization of synthetic cooperative systems is still in its infancy, especially with respect to applications in catalysis. Only relatively recently has the targeted design of adaptive, cooperative ligand frameworks been recognized as a promising way to approach synthetic problems related to the selective conversion of substrates and the uncovering of new reactivity and previously unknown transformations.

This microreview is intended to survey four bioinspired strategies (Scheme 1) to induce and utilize cooperative reactivity in the context of (small molecule) substrate activation and homogeneous catalysis. Attention will be given to the use of redox-noninnocent ligands, to ligand–metal bifunctional substrate activation, to favorable interactions in bimetallic complexes and to adaptive, hemilabile coordination strategies. Particular emphasis on recent and ongoing efforts to combine these design concepts with earth-abundant late transition metals (Fe, Co, Ni and Cu). The nascent research field of supramolecular cooperative catalysis is introduced separately at the end of this non-exhaustive but rather illustrative overview of this emerging research field.
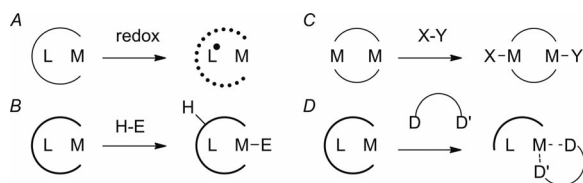
Scheme 1. Overview of cooperative reactivity strategies: *A* redox-noninnocent ligand scaffolds; *B* bifunctional substrate activation; *C* bimetallic substrate activation; *D* adaptive, hemilabile ligand coordination.

2. Cooperative Homogeneous Catalysis

One of the big focus points in present-day catalysis is the search for catalysts based on earth-abundant metals for green energy production and applications.[11] As such, the production of dihydrogen from a renewable resource like water and at low overpotentials, utilizing solar energy, is at the forefront of these developments. These attempts are driven by the desire to decipher ways to obviate the need for scarce, expensive Pt (electro)catalysts and to replace them with base-metal systems. Initial progress was made on the use of diiron systems as electrocatalysts for the reduction of protons to dihydrogen.[4] Even more timely and with pronounced usefulness for catalytic applications are ligand-metal assemblies that operate via an intramolecular acid/base functionality located in the ligand framework, akin to the hydrogenase active site.[12] The introduction of a biorelevant azadithiolate co-factor allowed the investigation of cooperative proton reduction events, involving intramolecular proton-hydride coupling processes to generate H_2 via a bifunctional pathway.

Ligand-assisted reactivity has so far proven particularly attractive for hydrogenation-related catalysis, involving het-erolytic H_2 activation as a key step in the overall processes. Most of these cooperative catalytic systems incorporate alcohol–ketone[14] or amine–amide functionalities.[15] Impressive catalytic activities and mechanistic insights have been obtained for a number of these bioinspired molecular systems and for various types of substrates.

These developments in turn allow for a wider range of activity than traditionally provided for by metal-based catalysis alone. However, the vast majority of catalytic systems developed and applied to date are based on expensive, noble metals. However, it is essential and thus believed to be only a matter of time before combinations of earth-abundant first-row transition metals and cooperative ligand scaffolds will show to be equally powerful as or even to surpass current noble metal based methodologies and will enable also completely new reactivity to be utilized in catalytic transformations.

2.1 Redox Noninnocent Systems

First-row transition metals often display one-electron reactivity rather than the more common two-electron pathways typically observed with second- and third-row analogues. However, the use of these earth-abundant metals in combination with ligand-based redox-activity is still underdeveloped in catalysis, as the main focus in the past decade has been on detailed understanding of electronic structures of both metal and ligand fragments in stoichiometric reactivity studies.[16,17,18] It is foreseen that these powerful combinations of both metal and ligand redox-noninnocent systems will lead to new catalytic reactions and improvements in existing processes.

Many different types of ligand scaffolds[19] have proven to engage in ligand-based redox-processes when coordinated to (late) transition metals, which often strongly complicates formal oxidation state assignments as well as the overall electronic structure determination of the resulting species. Well-known and thoroughly investigated examples of these so-called redox-noninnocent ligand systems include *inter alia* quinones, dithiolenes or α-dimines.[20] More recently, ligands such as bis(imino)pyridines, diphenylamine-based systems and even Fischer carbenes have been shown to be susceptible to redox-chemistry in the coordination sphere of a transition metal.
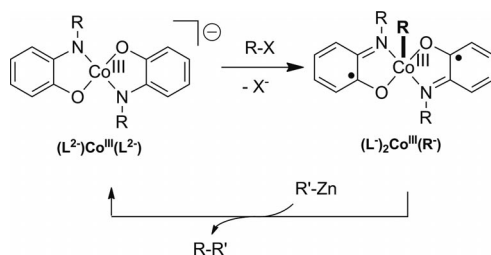
Bis(imino)pyridines have been shown to undergo ligand-based redox-events, which do not affect the formal oxidation state of the coordinated metal.[21] This makes scenarios possible wherein the electron storage capacity of ligands supplies the redox-equivalents necessary to drive reactions such as selective C–C bond formation in the hydrovinylation of alkenes and the cyclization of diynes with iron (Scheme 2).[22,23] As such, it is a very powerful type of catalytic approach, that may be expandable to other metals as well, such as cobalt.[24] Both the "oxidative addition" and "reductive elimination" processes associated with the two C–C bond forming processes lead to oxidation and reduction of the ligand rather than the metal (which stays in
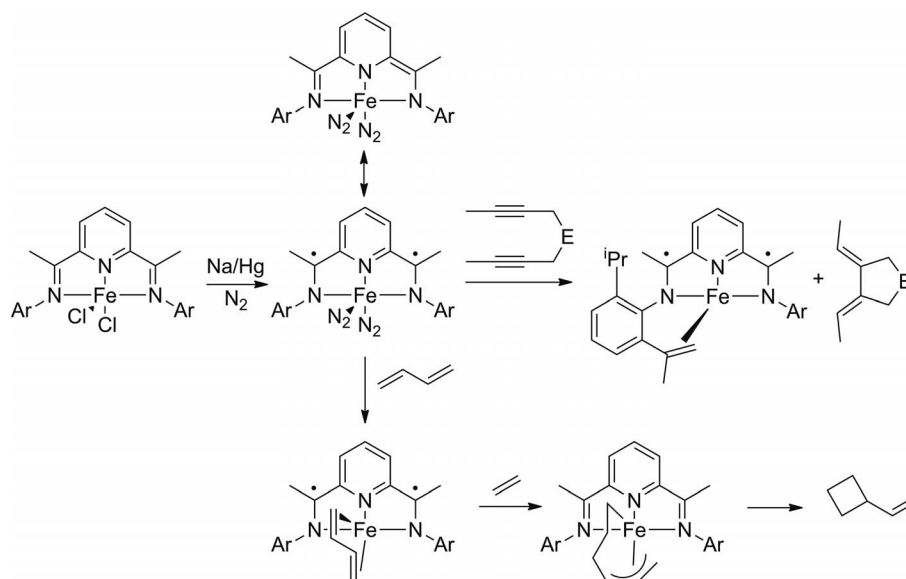
Scheme 2. Formation of a Fe complex based on bis(imino)pyridine and its reactivity in the cyclization and hydrovinylation of unsaturated hydrocarbons.

the Fe[II] spectroscopic oxidation state throughout the entire catalytic cycle), and thereby the redox-active bis(imino)-pyridine ligand imposes some noble character to iron. This concept is highly compelling and suggests that it could well be possible to replace noble metals currently used in several types of organometallic catalytic reactions by cheaper and more abundant first-row TM's (perhaps even main-group metals). The Chirik group has expanded the chemistry of Fe-based bis(imino)pyridine complexes also to hydrogenations, polymerizations and stoichiometric bond-activation reactions.[25]
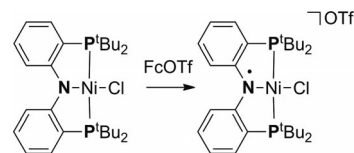
Soper and co-workers recently showed that metal-carbon bond formation can occur via metal-centered oxidative addition steps but *without* changing the d-electron configuration of the metal.[26] This was made possible by using redox active ligands that offer selective and fast electron transfer to the metal. The particular Co[III] complex, which is a *square-planar* Co[III] species (Scheme 3), featured two robust, redox noninnocent amidophenolate ligands. These ligands are easily, yet reversibly oxidized by one electron, thereby forming stable imino-semiquinone radical ligands. The (stoichiometric) cross-coupling of alkylzinc reagents with alkylhalides was demonstrated to be facilitated by this in-

novative "electron-borrowing" methodology. Eventually this could lead to cross-coupling transformations with earth-abundant metals instead of the expensive noble transition metals utilized extensively at the present time.

Mindiola has described the redox-activity of specific monoanionic PNP-pincer scaffolds.[27] Starting from neutral square-planar NiCl(PNP[iPr]), this species reacts with FcOTf (Fc = ferrocenium) to induce oxidation of the ligand backbone rather than the metal center (also certain Ag-salts are amenable to afford this redox-reaction), generating a ligand-centered radical anion coordinated to the unaltered square-planar Ni[II] center (Scheme 4). The electronic structure of this unusual complex was investigated via a combined X-ray crystallographic, spectroscopic (UV, EPR, multi-edge XAS) and computational DFT study, indicating that the radical character is most pronounced at the nitrogen atom, with further contributions from the two phenyl rings. Although the authors speculate on the usefulness of this ligand based redox-switching event for catalysis, no further investigations on this matter have been reported to date. It is likely that this type of ligand cooperativity may find applications in certain types of bond activation processes, potentially even with further functionalization.

Scheme 3. Schematic representation of the "electron borrowing" methodology of redox-active amidophenolate ligands coordinated to a Co[III] metal center.

Scheme 4. Redox noninnocent behaviour of diphenylamide derived PNP ligand when coordinated to Ni[II].

It may be speculated that the all-nitrogen donor NNN analogues[28] also facilitate such ligand-centered redox-behaviour during e.g. Ni-catalyzed Kumada coupling of alkyl

Grignards and alkyl halides rather than going proceeding through the intermediacy of a formal Ni[IV] species.[29] It was recently established that the same nickel catalyzed cross-coupling reactions using related bidentate NN analogues followed a radical mechanism.[30]

The group of Zhang recently introduced Co[II](por*) complexes, wherein por* represents C_2-symmetric porphyrins functionalized with chiral auxiliaries that are also able to interact with suitable substrates via H-bonding.[31] This has resulted in unprecedented high enantioselectivity for the Co[II]-catalyzed cyclopropanation of electron-poor alkenes with diazoesters.[32] It was subsequently established, through combined spectroscopic and theoretical studies using ethyl diazoacetate as model substrate, that the relevant cobalt(carbene) intermediate displays radical character at the carbene carbon atom rather than the d^7 cobalt center, making it a one-electron reduced Fischer carbene (Scheme 5). This effectively implied that metal-carbenes can display redox-noninnocent behaviour.[33] Subsequent computational investigations have identified ligand-based radical reactivity in the strongly related aziridination of electron-poor alkenes with azides {as well as PhI = NTs – [N-(p-tolylsulfonyl)imino]phenyl-iodinane} as nitrene source.[34] Follow-up reactivity studies will establish if this observed noninnocence in these neutral ligand fragments, previously thought to be mere innocent substrates or spectator ligands at best, will reach beyond these C–H and C=C bond activation reactions. It can be envisioned that one-electron reduced Fisher or one-electron oxidized Schrock carbenes could lead to alternative reaction pathways for various reactions, also toward C–heteroatom bond formation processes. For the moment, the limited accessibility of suitable precursors for these carbenes (diazo compounds) and nitrenes (PhINTs or azides) might hamper progress, unless ways are found to convert alkyl or amine fragments into the corresponding six-valence electron species. These elegant systems could be regarded as examples of supramolecular cooperative catalysis, given the strong influence of the H-bonding motif between the ligand periphery and the substrate, both with respect to enantiodiscrimination and stabilization of the radical nature of the carbene fragment.

2.2 Bifunctional Substrate Activation

Pincer ligands have been studied intensively ever since their inception in the 1970's by Shaw.[35] Many variations of these rigid, meridional tridentate ligand scaffolds have been developed, including many that do not exhibit rigid pincer-like binding characteristics but induce a more flexible coordination sphere around the metal center of choice.[36] The original design featured a central (pivotal) deprotonated sp^2 carbon flanked by two heteroatom donor groups, but over the years various other classes have emerged, the latest being EBE with a deprotonated boryl group.[37] Formally neutral tridentate pincer ligand systems have become very popular in the last decade(s), such as those based on 2,6-diaminopyridine[38] or 2,6-dihydroxypyridine.[39] They offer complementary chemistry to their monoanionic derivatives, e.g. when focusing on low-valent metal centers (e.g. Rh[I], Ir[I]) or if coordinatively unsaturated dicationic complexes (such as Pt[II]) are targeted.

Recently, a specific class of aromatic, neutral tridentate ligands based on lutidine, and close analogues thereof, has received much attention. One special feature of these 2,6-lutidine-derived systems is their ease of deprotonation of the methylene spacer group, effectively making this a "noninnocent" class of ligands.[40] The mode of action and type of reactions accessible with this kind of ligand-metal cooperative reactivity differs significantly from that observed in previously studied acid/base switching systems. Other types of deprotonatable ligand structures have appeared in the literature in recent years, but again research initially focussed mainly on proven second- and third-row group 8–10 transition metals, which will not be further discussed here.[41]

Given the cooperative nature of the lutidine-derived **PNP[R]** class of ligands and their close PNN analogues, which was elegantly utilized for stoichiometric reactivity and catalytic transformations using second- and third-row transition metals,[40] it is somewhat remarkable to notice that only very recently the first reports of first-row transition metal based chemistry with this reactive type of scaffold was reported. Mononuclear Fe[II] and Fe[0] complexes were investigated by Milstein,[42] Goldman[43] and Chirik.[44] Interestingly, subtle but significant differences were noted in the actual geometry around the Fe-center, depending on the substitution on the phosphane side-groups (Scheme 6). With the sterically less encumbered ligand PNP[iPr], the Fe center shows a trigonal bipyramidal structure, while for the bulkier analogue PNP[tBu] a square-pyramidal geometry is obtained, both for the Fe[II] as well as the formal Fe[0] state.

To date, only one example of cooperative catalysis with Fe has been detailed using this type of ligand framework (Scheme 7).[45] The hydrogenation of ketones was reported
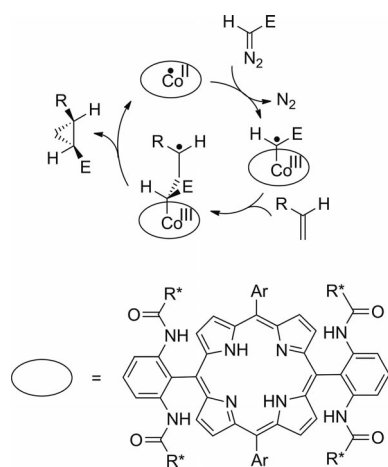
Scheme 5. Co-catalyzed asymmetric cyclopropanation of electron-poor alkenes occurs via carbene radical anion species, with aided stability provided by a functionalized chiral porphyrin.
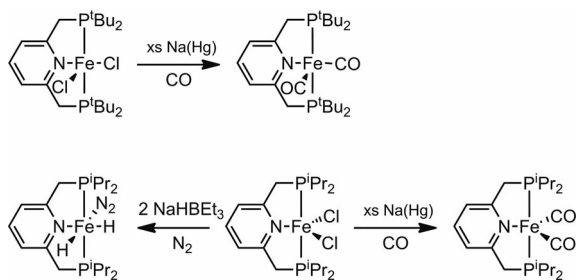
Scheme 6. Subtle influence of the R group in **PNP^R** on the geometry of the Fe complex.

to be quite efficient with [FeBr(H)(CO)(**PNP^{tBu}**)] as precursor and speculated to behave in a cooperative manner, reminiscent to the classic Noyori-type mechanism. As iron-catalyzed hydrogenations are gaining in importance, due to the obvious advantages gained over other more established metals,[46] it is expected that various types of ligand scaffolds will be successfully probed to display reactivity toward susceptible C=C and C=X groups (X = O, N).
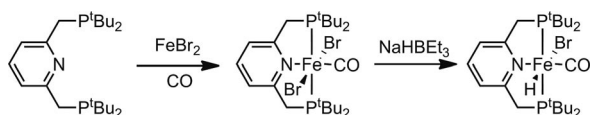

Scheme 7. Preparation of Fe(Br)(H)(CO)(**PNP^{tBu}**), which is a catalyst for the cooperative hydrogenation of ketones.

Chemistry and catalytic reactivity of nickel with cooperative ligand-scaffolds is still far from developed. Initial results using the same **PNP^{tBu}** framework as for Fe (vide supra) have been obtained starting from dicationic Ni^{II} precursors via a sequential dearomatization-reprotonation protocol to generate terminal thiolate complexes as well as nickel-alkyl species (Scheme 8).[47] Nickel alkyl complexes are inferred as catalytic intermediates for a range of organic transformations, such as hydrovinylation, Heck and Kumada coupling and polymerization reactions. Their targeted synthesis, via sequential ligand-based activation and metal-based substitution reactions, in combination with dual-mode reactivity options at both ligand and metal *and* the potential to switch the catalyst on or off during catalysis might aid the development of more active or selective systems.
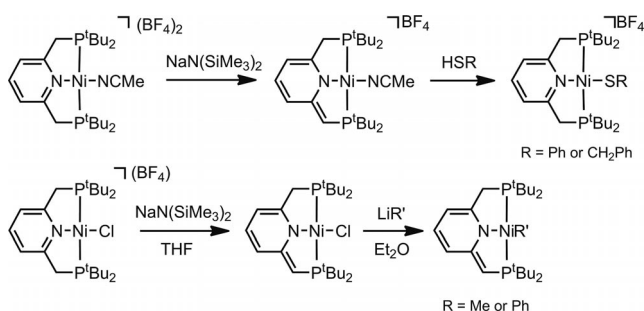

Scheme 8. Synthesis of the Ni-alkyl complexes featuring a deprotonated version of ligand **PNP^{tBu}**.

The first example of hemilability of the central N-atom of the cooperative, neutral pincer ligand **PNP^{tBu}** was recently discussed; pyridyl nitrogen coordination could be monitored using IR spectroscopy and was shown to be dependent on charge as well as steric arguments (Scheme 9).[48] Only in case of a cationic species was N-coordination observed. Furthermore, selective alkylation of the dearomatized ligand backbone {obtained after treatment of the complex [CuBr(**PNP^{tBu}**)] with base} was described, highlighting the reactive nature of these charge-switching scaffolds.[49] This might lead to new opportunities for the synthesis and exploration of modified, perhaps even chiral analogues of this cooperative ligand scaffold.
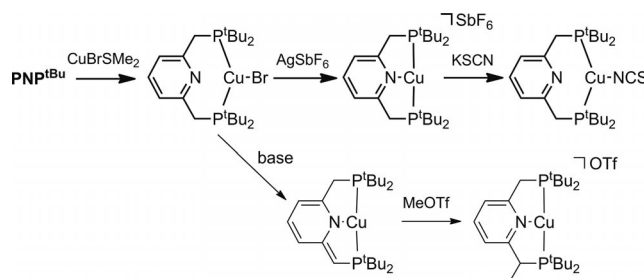
Scheme 9. Hemilabile coordination and reactivity of the dearomatized T-shaped complex Cu(**PN–P^{tBu}**) with electrophiles.

Apart from the preferred coordination as a typical meridional, tridentate "pincer" ligand, recent evidence from X-ray crystallography proved that this framework can also act as a dinucleating scaffold, bridging two Cu^I centers in an unprecedented κ^2–P,N-κ^1–P mode (Scheme 10).[50] We recently demonstrated the use of these Cu complexes with cooperative PNP-ligands to be active in the [2+3] dipolar addition reaction between azides and alkynes. The intermediacy of complex **2** was strongly suggested by stoichiometric reactivity studies. Initial formation of a phenyl acetylide derivative after reaction of complex **2** with HCCPh (the acetylenic proton is acidic enough to reprotonate the dearomatized ligand) and subsequent addition of benzyl azide led to generation of the triazole product through intramolecular ligand-to-triazole proton transfer.[51]
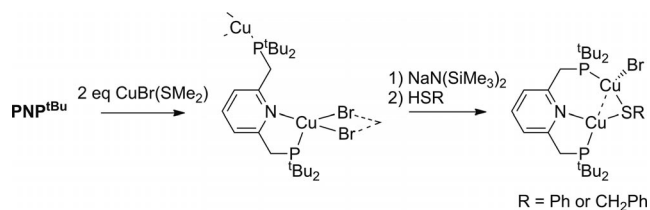
Scheme 10. Generation of unusual dinuclear Cu^I complexes with a bridging **PNP^{tBu}** ligand via sequential dearomatization-reprotonation.

Besides reversible deprotonation or dearomatization in order to induce cooperative reactivity, some systems can act as intramolecular base in tandem with first-row transition metals, much like the classic Noyori Ru-catalysts.[13,52] This concept is e.g. explored in the context of hydrogenase modeling. DuBois and co-workers have employed bioinspired

bis(phosphanylmethyl)amines to play a crucial cooperative role during the generation of dihydrogen at mononuclear Co[II] and Ni[II] centers (Scheme 11).[53] Square-planar starting compounds carrying either one or two PNP ligands have been prepared, whereby the cooperating ligand furnishes a proton-accepting pocket in close proximity to an axial coordination site at the metal center, that may bind a hydride. Two sequential proton-coupled electron transfer steps furnish the hydride-ammonium species that can lead to the formation of H_2.
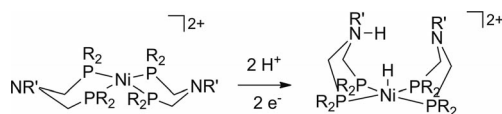

Scheme 11. Cooperative production of dihydrogen through bifunctional proton activation.

The same catalyst system has subsequently been covalently anchored and immobilized on electron-conducting carbon nanotubes by the group of Palacin, Fontecave and Artero, who demonstrated the highly efficient use of these devices in the reversible oxidation of H_2, with turnovers of up to 100,000 at very low overpotentials.[54] In subsequent work the non-covalent adsorption onto carbon nanotubes using pyrene-functionalized PNP scaffolds was shown.[55]

Recently, the groups of Holland and Eisenberg demonstrated the photocatalytic production of dihydrogen from water using this type of Ni complexes featuring cooperative ligands.[56] It is clear that the combination of an intramolecular proton-docking site close to an hydridophilic metal site creates a powerful cooperative combination for this deceptively simple but complex reaction, as it reduces the required overpotential needed to drive this reaction. It is paramount for the development of catalysts and devices for solar fuel production to utilize and incorporate the same principles.

The group of Talarmin, Schollhammer and Gloaguen has reported on a diphosphanyl-amine ligand resembling the naturally occurring azadithiolate co-factor with regards to its potential for proton-binding whilst being in close proximity to a metal-hydride site.[57] This PNP-system can act as a bridging or a chelating ligand (depending on reaction conditions) to a diiron system reminiscent of the [Fe₂]-H₂-ase active site (Scheme 12). Addition of acids to this biomimetic model system led to initial protonation at the intramolecular basic nitrogen, with subsequent proton-transfer to the diiron core.
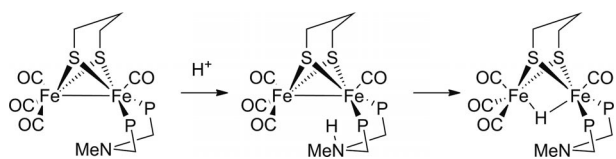
Scheme 12. Cooperative proton-transfer within a bioinspired diiron model system relevant for H2ase activity.

Recently, a new twist to this strategy was presented by the group of Ott.[58] Using a particular *mononuclear* Fe[II] system featuring a chelating dithiolate ligand (Scheme 13), which in itself is already noteworthy, they observed that one of the thiolate-sulfur atoms could be reversibly protonated. This example of ligand reactivity was then used to facilitate cooperative dihydrogen production. Electrocatalytic proton reduction was shown to be very efficient at relatively low overpotentials.
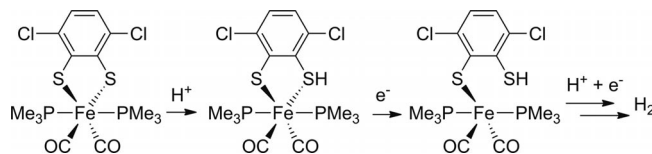

Scheme 13. Cooperative (noninnocent) reactivity of a dithiolate ligand on a mononuclear Fe[II] species, relevant for bioinspired dihydrogen production.

2.3 Bimetallic Catalysis

Cooperativity in a di- or polynuclear metal system is mainly useful and productive if the activity exhibited by the multimetallic core either surpasses results obtained for the mononuclear analogue or if the cluster induces a reactivity that is not possible otherwise.[59] For some time now, bimetallic cooperative catalysis has been established in the field of polymer catalysis, with landmark contributions by the group of Coates on CO_2-propylene oxide copolymerization systems that outperform their mononuclear analogues.[60] Jacobsen pioneered the use of dicobalt species for the ring opening of epoxides.[61] Recently, some adaptations of this proven concept have been elaborated on, using supramolecular bowl-shaped structures.[62] The area of "click chemistry", originally defined by Sharpless[63] to include 100% atom-efficient, thermodynamically favored and very selective coupling reactions between two reactive coupling partners, is dominated by the copper-catalyzed azide–alkyne coupling to generate bioorthogonal triazole fragments. The group of Marks has made elegant contributions using well-designed dinickel complexes based on dinucleating phenoxyiminato ligands, which were shown to induce cooperative catalysis in both the homopolymerization of ethylene *and* the copolymerization of ethylene with polar comonomers (norbornadiene and acrylates).[64] This has led to high levels of comonomer incorporation, significantly higher branch-content in PE and hence in different polymer microstructures. Meyer has developed innovative dinucleating ligands based on functionalized pyrazolate scaffolds and the corresponding Ni, Cu and Zn bimetallic complexes thereof, which are active models for urease (Ni),[65] phosphatase (Zn)[66] and e.g. polyphenolether synthesis (Cu).[67,68]

Ozerov has described the formation of specific Pd[I](PNP) dimers – PNP = bis[2-(diisopropyl- phosphanyl)-4-methylphenyl]amido – via photolytic activation of the corresponding mononuclear Pd(PNP)(alkyl) species and utilized these systems (Scheme 14), which feature an unsupported

Pd–Pd single bond and can thus be viewed as two-electron reductants, for the bimetallic, homolytic activation of particular H–E bonds, most notably H_2O and NH_3.[69] It remains to be seen if similar strategies may be fruitful with first-row analogues, especially in combination with redox-active ligands (vide infra).
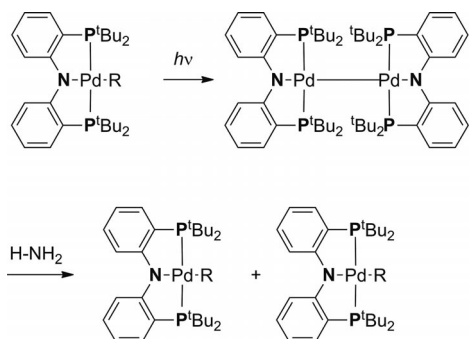
Scheme 14. Dinuclear activation of ammonia at a Pd^I–Pd^I dimer.

Peters has developed dinuclear copper species based on the same PNP ligand scaffold as well as its close structural PPP derivative [PPP = bis(2-diisopropylphosphanyl)phenylphosphane],[80] which showed very interesting electronic behaviour, allowing the isolation of mixed-valent states as well as spectacular, long-lived luminescence.[71,72] Using the same PNP framework (Scheme 15), Mindiola disclosed the synthesis and follow-up reduction of the mononuclear CoCl(PNP) complex, which revealed some interesting chemistry, most notably the fact that the one-electron reduced Co^I species Co(PNP) rapidly dimerized, with the PNP ligand acting as a bridging dinucleating scaffold in the resulting diamanoid structure.[73] Under an atmosphere of CO, the related mononuclear species was again obtained. When the reduction was performed under an N_2 atmosphere, the end-on coordinated dinuclear dinitrogen complex could be isolated. To date, no further reactivity with any these species has been reported; it can be expected that ultimately these types of species may be utilized for dinitrogen functionalization.
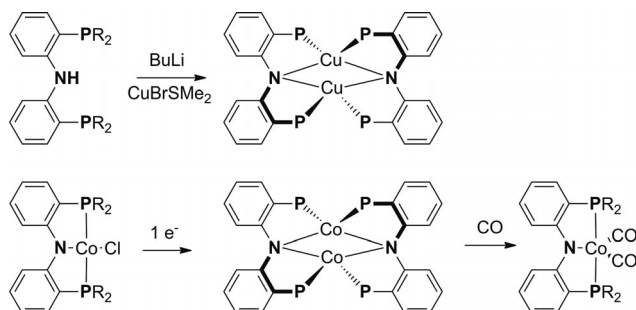
Scheme 15. Formation of dinuclear Cu^I and Co^I species with a bridging PNP ligand.

The group of Agapie recently adapted the ligand backbone design, originally described by Vilar[74] to prepare mono- and dinuclear Pd^I complexes, based on terphenylphosphanes in order to arrive at dinuclear Ni^I-dimeric systems facilitate stoichiometric C–C bond formation reac-

tions between bis(orthometallated) biphenyls and CO (Scheme 16).[75] The two Ni-centers actively cooperate during the essential steps of this transformation, and one potential mechanism includes formal two-electron reduction of the Ni^I-dimer core after initial association and insertion of CO in a Ni–C bond. Indeed, dinuclear Ni^0 species have been observed in the reaction mixture. Strikingly, the same dinickel biphenyldiyl complex was also reactive toward geminal dichloroalkanes, leading to the formation of substituted fluorenes. This suggests an oxidative mechanism for the dinickel core, with oxidative C–Cl addition over the metal-metal bond as one option (radical mechanisms to form mixed-valent Ni^I–Ni^{II} species are another viable possibility). Therefore, there seems to be much versatility in the type of bimetallic scaffolds and the electronic state of the metal–metal bond to induce selective bond forming reactions. Key aspect for further development is the transformation from stoichiometric to catalytic turnover, with regeneration of the active dinickel species. Furthermore, it is potentially also possible that such dimers actually break up into reactive mononuclear entities. Similar dinuclear nickel species and their reactivity were reported by the groups of Hillhouse and Johnson very recently.[76]
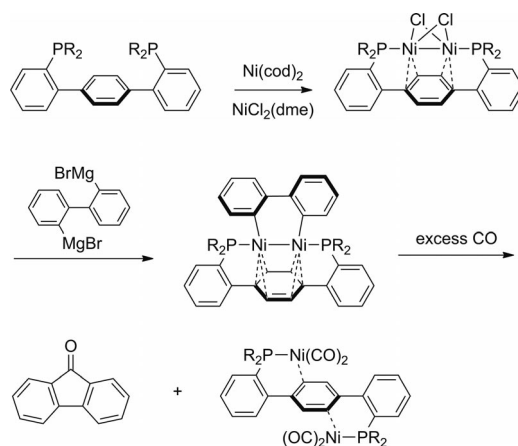
Scheme 16. Formation and C–C bond forming reactivity of a dinuclear Ni^I–Ni^I complex with a *trans*-spanning terphenyldiphosphane ligand (xs = excess).

Betley has reported elegant polydentate, C_3-symmetric[77] hexaamine ligand design strategies to prepare tri- and hexanuclear iron clusters.[78] The former was shown to be a suitable platform for the generation of nucleophilic μ^3-nitrido species that smoothly reacted with MeI to generate the corresponding methylimide. The iron centers in the hexanuclear clusters showed a high level of electronic cooperativity, which translated into a highly delocalized electronic structure of the Fe ions. The stoichiometric reduction of NO_2 was described, which indicates that reactivity is possible with these clusters, concomitant with noticeable structural changes to the hexanuclear geometry.[78d] These bioinspired clusters may prove useful for small molecule activation, in the spirit of e.g. nitrogenase or as homogeneous models for heterogeneous catalysis such as the Haber-Bosch process.[79] The group of Agapie has reported on similar polynuclear

clusters accommodated by polydentate ligand scaffolds and the resulting electronic communication between the metal centers.[80]

Bouwman et al. recently showed that CO_2 can be reductively coupled to form oxalate using a dinuclear Cu^I species, wherein each copper center has an N_3S coordination sphere, with the two metal centers bridged merely by a disulfide linkage (Scheme 17).[81] This system showed remarkable selectivity for CO_2 over O_2 and regeneration of the active precursor was feasible through electrocatalytic reduction. The proposed mechanism involves initial reduction of CO_2 in the coordination sphere of Cu^I to the $CO_2^{\cdot-}$ radical ion, which occurs at a significantly lower potential than for the non-metal mediated process, concomitant formation of Cu^{II}. Dimerization (with generation of a tetranuclear copper-species) results in oxalate formation, which could be liberated from the Cu_4 core by addition of Li salt.
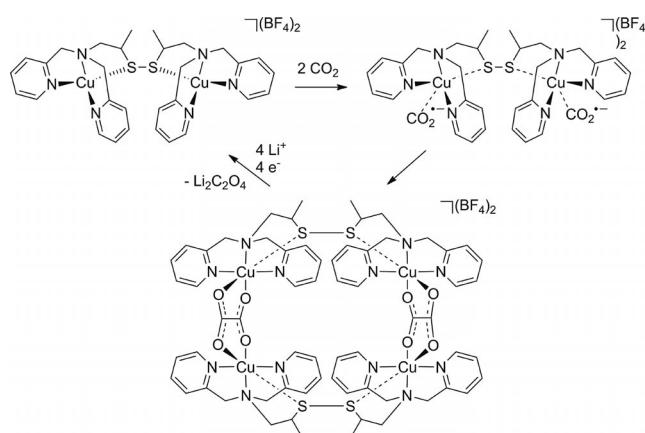

Scheme 17. Reductive coupling of CO_2 to oxalate by a dinuclear Cu^I complex.

2.4 Hemilabile Ligands for Cooperative Catalysis

Biology often employs donor groups and ligating fragments that show variable coordination to the metal center. This adaptive coordination behaviour (termed hemilability or flexidenticity)[82] allows the regulation of vacant sites and the selective conversion of reactive substrates. Adaptive ligand systems that can accommodate different stages for a catalytically active complex during turnover, e.g. creating and masking vacant sites depending on external stimuli (reagents, substrates) are very promising to induce selective cooperative catalysis, provided the characteristics of the hemilabile group can be properly tuned. The group of Braunstein has developed many bi- and tridentate scaffolds that feature weakly coordinating donor groups, which easily dissociate from the metal center in the presence of exogenous ligand or substrate.[83]

Allosteric catalysis on the basis of hemilabile coordination of a hybrid ligand to a secondary metal site, whereafter a nearby primary catalytic site is transformed from a dormant to an active catalyst state, has been demonstrated by Mirkin and co-workers in a number of systems.[84] They

developed cleft-like dinuclear systems that operate via a "weak-link" concept based on P,S-ligation to a transition metal (typically Rh), that is connected to a first-row metal based (Mn, Zn) catalyst site (Scheme 18). One of their elegant designs features two Mn-salen units sandwiched between these P,S-ligated Rh hinges. Introduction of an exogenous substrate resulting in opening of the cleft, which led to higher accessibility of the bis-Mn-salen core and subsequently to catalytic activity in the acyl transfer reaction involving acetic anhydride and pyridyl carbinol as the substrates, generating acetate as product. Furthermore, a system was devised where this product was the exogenous trigger to induce catalyst activity (autocatalysis). More recently, triple-decker catalytic systems have been developed, wherein two side-arm functionalities act as "hinges" to selectively mask the catalytically active metal site, which was an Al-salen unit capable of catalyzing the ring-opening of ε-caprolactone.[85]
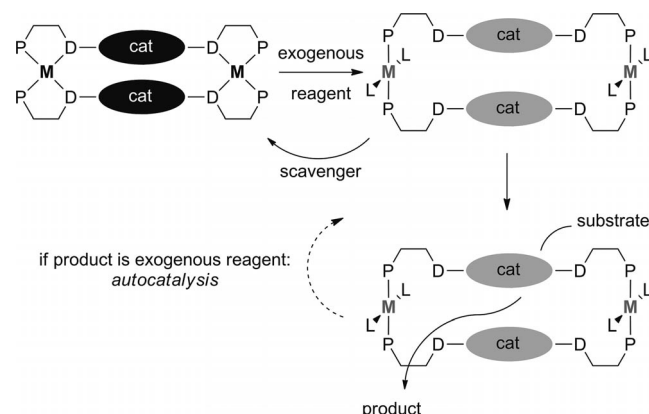
Scheme 18. Mechanism of autocatalysis at a primary catalytic site made possible by selective hemilabile coordination at a secondary metal site.

Recently, new hybrid meridional tridentate ligands have been introduced, that feature two distinctly different side-arm donor groups. The use of such hemilabile *pincer* ligands was pioneered by Milstein, who developed neutral hybrid PNN systems that were amenable to induce unprecedented dehydrogenative coupling reactions involving alcohols.[86] Also hybrid, asymmetrically substituted monoanionic ligands have been developed that display selective dissociation of one of the side-arms, thereby vacating a coordination site at the metal center (Scheme 19).[87] To
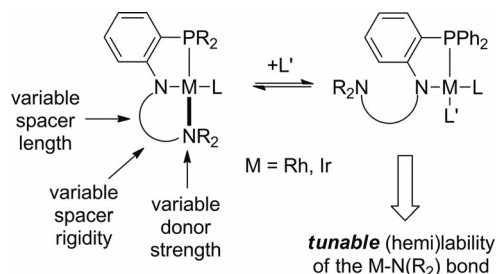
Scheme 19. Concept of tunable hemilability to induce cooperative reactivity.

date, this ligand design has not been combined with first-row transition metals but has only been tested with Rh, Ir and Ru.

3. Supramolecular Cooperative Catalysis

Supramolecular catalysis is a rapidly expanding field within homogeneous catalysis, wherein self-assembly via non-covalent interactions (i.e. H-bonding, metal templation, anion templation or other types of weak interactions) is employed to construct the desired ligand scaffold and/or to generate the supramolecular catalyst species. This also includes examples dealing with self-complementary mono-phosphorus ligands.[88] To date, this concept has been mainly explored with second- and third-row metals, although first-row metals such as Zn or Cu are frequently employed as metal template.[89] However, merging this strategy with ligand based noninnocence has been ill-explored to date.

Apart from the system of Zhang (vide supra), only a few ligand scaffolds combine non-covalent ligand-substrate interactions with first-row transition metal complexes. Borovik and co-workers developed tripodal ligand scaffolds adorned with H-bonding patterns along the periphery.[90] These ligands have allowed the selective construction of e.g. Fe-oxo and Co-hydroxo species, wherein the oxygen-containing fragment is stabilized by H-bonding to the amide units in the ligand side-arms. This may ultimately be a useful strategy for selective catalytic oxygenation or oxidation reactions.

Breit and co-workers reported on the Ni-catalyzed hydrocyanation of styrenes using self-assembled bidentate phosphane ligands.[91] Although this provides a very elegant way to prepare new ligand systems, with the advantage of creating larger libraries due to the higher availability of building blocks, the self-assembly does not extend to the level of cooperative catalysis, as the ligands do not actively participate during substrate conversion but are merely configured using non-covalent H-bonding interactions. In general, despite the "synzymatic" nature of some of these supramolecular catalysts, there is no true cooperative aspect as yet incorporated in most of these concepts, nor are first-row transition metals exploited in this way. However, it is envisioned that such favorable design features may well come into existence in the near future, as more control over the preparation and behaviour of these supramolecular systems is gained.[92]

Crabtree and Brudvig developed a Mn-based oxidation catalyst for C–H oxygenation reactions, wherein substrate recognition and preorganization induced by multiple hydrogen bonding were essential to achieve the observed high chemoselectivity.[93] The bimetallic catalyst featured a bioinspired Mn_2 reactive center with bridging oxo-ligands and a functionalized terpyridyl ligand adorned with a carboxylic acid moiety capable of interacting with the carboxylic acid group of the substrate ibuprofen, thereby positioning the desired C–H bond directly above the active Mn_2 center.

Control experiments supported the role of hydrogen bonding in orienting the substrate to achieve high selectivity.

The use of other types of cooperative ligand structures so far has been limited to noble metal chemistry. For instance, the elegant systems employed by the group of Jun[94] and Breit et al.,[95] wherein the ligand interacts strongly with the substrate of choice – be it an aldehyde to infer selective hydroacylation, through the formation of a reversible imine bond, or the hydroformylation of α,β-unsaturated carboxylic acids, making use of directing H-bonding – have been tested mainly with Rh and Ru. Related approaches using bifunctional substrate activation have been developed by Reek et al., wherein hydrogen bonding interactions[96] between the ligands and the substrates were shown to enhance the asymmetric hydrogenation of functionalized substrates. The use of an anion-binding pocket as the backbone of a diphosphorus ligand was able to regulate the regioselectivity during the rhodium-catalyzed hydroformylation of unsaturated carboxylate substrates.[97]

In general, despite the obvious advances developed and the complementary or beneficial aspects of various complex or supramolecular (cooperative) systems recently reports, e.g. in terms of reactivity, tunability and selectivity, to date no attention is given at all to applying these concepts with first-row metals and there is a whole field waiting to be explored.

4. Conclusions

The field of transition metal cooperative catalysis has seen much fascinating progress in the last decade, but the first-row transition metals are still far from well-developed in this respect. It is believed that combining cooperative ligands, either featuring redox-activity, proton-transfer abilities or coordinative adaptivity with earth-abundant metals such as Fe, Co, Ni or Cu, either as mononuclear or bimetallic species, will prove to be very efficient for both new reactivity as well as the use of cheap metals for noble tasks. This will include processes to facilitate the cooperative, catalytic activation and functionalization of small molecules for which currently no methodologies are available or that can only be mediated by expensive metals.[98,99,100]

Acknowledgments

[1] a) I. Bertini, H. B. Gray, S. J. Lippard, J. S. Valentine, *Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, **1994**.

[2] a) J. Stubbe, W. A. van der Donk, *Chem. Rev.* **1998**, *98*, 705–762; b) G. Parkin, *Chem. Rev.* **2004**, *104*, 699–768; c) J. Weston, *Chem. Rev.* **2005**, *105*, 2151–2174; d) D. Voet, J. G. Voet, *Biochemistry*, Wiley, New York, **2008**.

[3] a) N. Ito, S. E. V. Phillips, C. Stevens, Z. B. Ogel, M. J. McPherson, J. N. Keen, K. D. S. Yadav, P. F. Knowles, *Nature* **1991**, *350*, 87–90; b) N. Ito, S. E. V. Phillips, K. D. S. Yadav, P. F. Knowles, *J. Mol. Biol.* **1994**, *238*, 794–814; c) Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537–540; d) J. Müller, T. Weyhermüller, E. Bill, P. Hildebrandt, L. Ould-Moussa, T. Glaser, K. Wieghardt, *Angew. Chem.* **1998**, *110*, 637; *Angew. Chem. Int. Ed.* **1998**, *37*, 616–619; e) J. W. Whittaker, *Chem. Rev.* **2003**, *103*, 2347–2363.

[4] For natural systems, see: a) P. M. Vignais, B. Billoud, *Chem. Rev.* **2007**, *107*, 4206–4272; b) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.* **2007**, *107*, 4273–4303. For model systems, see: c) C. Mealli, T. B. Rauchfuss, *Angew. Chem.* **2007**, *119*, 9100; *Angew. Chem. Int. Ed.* **2007**, *46*, 8942–8944; d) F. Gloaguen, T. B. Rauchfuss, *Chem. Soc. Rev.* **2009**, *38*, 100–108; e) C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274.

[5] For recent reviews, see: a) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, *Chem. Soc. Rev.* **2006**, *35*, 814–840; b) J. I. van der Vlugt, F. Meyer, *Top. Organomet. Chem.* **2007**, *22*, 191–240; for a recent model system, see: c) M. Rolff, J. N. Hamann, F. Tuczek, *Angew. Chem. Int. Ed.* **2011**, *50*, 6924–6927.

[6] Such as sMMO, see: a) A. C. Rosenzweig, C. A. Frederick, S. J. Lippard, P. Nordlund, *Nature* **1993**, *366*, 537–543; b) B. J. Wallar, J. D. Lipscomb, *Chem. Rev.* **1996**, *96*, 2625–2657; c) S. Friedle, E. Reisner, S. J. Lippard, *Chem. Soc. Rev.* **2010**, *39*, 2768–2779; d) C. E. Tinberg, S. J. Lippard, *Acc. Chem. Res.* **2011**, *44*, 280–288. For a bioinspired NiFe system, see: S. Yao, C. Herwig, Y. Xiong, A. Company, E. Bill, C. Limberg, M. Driess, *Angew. Chem. Int. Ed.* **2010**, *49*, 7054–7058.

[7] a) J. S. Rieske, D. H. MacLennan, R. Coleman, *Biochem. Biophys. Res. Commun.* **1964**, *15*, 338–344; b) J. S. Rieske, *J. Biol. Chem.* **1968**, *239*, 3017–3022; c) T. A. Link, O. M. Hatzfeld, M. Saynovits, in *Bioinorganic Chemistry* (Ed.: A. X. Trautwien), Wiley-VCH, Weinheim, Germany, **1997**, p. 312–325. For a synthetic structural model, see: J. C. Ballmann, A. Albers, S. Demeshko, S. Dechert, E. Bill, E. Bothe, U. Ryde, F. Meyer, *Angew. Chem.* **2008**, *120*, 9680; *Angew. Chem. Int. Ed.* **2008**, *47*, 9537–9541. For a functional model, see: K. Chen, L. Que Jr., *Angew. Chem.* **1999**, *111*, 2365; *Angew. Chem. Int. Ed.* **1999**, *38*, 2227–2229.

[8] J. I. van der Vlugt, F. Meyer, *Met. Ions Life Sci.* **2007**, *2*, 181–240.

[9] a) I. Bertini, A. Sigel, H. Sigel, *Handbook on Metalloproteins*, Marcel Dekker, New York, **2001**; b) R. C. Linck, T. B. Rauchfuss, in: *Bioorganometallics* (Ed.: G. Jaouen), Wiley-VCH, Weinheim, Germany, **2005**.

[10] a) T. G. Traylor, C. K. Chang, J. Geibel, A. Berzinis, T. Mincey, J. Cannon, *J. Am. Chem. Soc.* **1979**, *101*, 6716–6731; b) E. B. Springman, E. L. Angleton, H. Birkedal-Hansen, H. E. van Wart, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 364–368; c) H. E. van Wart, H. Birkedal-Hansen, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 5578–5582; d) J. Wuerges, J.-W. Lee, Y.-I. Yim, H.-S. Yim, S.-O. Kang, K. Djinovic Carugo, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 8569–8574; e) D. P. Barondeau, C. J. Kassmann, C. K. Bruns, J. A. Tainer, E. D. Getzoff, *Biochemistry* **2004**, *43*, 8038–8047.

[11] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735.

[12] a) A. Silakov, B. Wenk, E. J. Reijerse, W. Lubitz, *Phys. Chem. Chem. Phys.* **2009**, *11*, 6592–6599; b) O. F. Erdem, L. Schwartz, M. Stein, A. Silakov, S. Kaur-Ghumaan, P. Huang, S. Ott, E. J.

Reijerse, W. Lubitz, *Angew. Chem. Int. Ed.* **2011**, *50*, 1439–1443. For some relevant structural and functional models of the Fe_2H_2ase, see: c) C. A. Boyke, J. I. van der Vlugt, T. B. Rauchfuss, S. R. Wilson, G. Zampella, L. De Gioia, *J. Am. Chem. Soc.* **2005**, *127*, 11010–11018; d) J. I. van der Vlugt, T. B. Rauchfuss, C. M. Whaley, S. R. Wilson, *J. Am. Chem. Soc.* **2005**, *127*, 16012–16013; e) J. I. van der Vlugt, T. B. Rauchfuss, S. R. Wilson, *Chem. Eur. J.* **2006**, *12*, 90–98; f) A. K. Justice, G. Zampella, L. De Gioia, T. B. Rauchfuss, J. I. van der Vlugt, S. R. Wilson, *Inorg. Chem.* **2007**, *46*, 1655–1664; g) F. Wang, M. Wang, X. Liu, K. Jin, W. Dong, G. Li, B. Åkermark, L. Sun, *Chem. Commun.* **2005**, 3221–3223; for a recent dicobalt-catalyst, see: N. K. Szymczak, L. A. Berben, J. C. Peters, *Chem. Commun.* **2009**, 6729–6731.

[13] Breakthrough examples and reviews: a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40; *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73; b) D. B. Grotjahn, *Chem. Eur. J.* **2005**, *11*, 7146–7153; c) M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788–789; d) F. W. Patureau, M. Kuil, A. J. Sandee, J. N. H. Reek, *Angew. Chem.* **2008**, *120*, 3224; *Angew. Chem. Int. Ed.* **2008**, *47*, 3180–3183; e) T. Zweifel, J.-V. Naubron, J. Grützmacher, *Angew. Chem.* **2009**, *121*, 567; *Angew. Chem. Int. Ed.* **2009**, *48*, 559–563; f) 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; g) Y. Kashiwame, S. Kuwata, T. Ikariya, *Chem. Eur. J.* **2010**, *16*, 766–770.

[14] a) Y. Blum, D. Czarkie, Y. Rahamim, Y. Shvo, *Organometallics* **1985**, *4*, 1459–1461; b) A. L. E. Larsson, B. A. Persson, J.-E. Bäckvall, *Angew. Chem.* **1997**, *109*, 1256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1211–1212; c) J. S. M. Samec, A. H. Éll, J. B. Åberg, T. Privalov, L. Eriksson, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2006**, *128*, 14293–14305; d) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2007**, *129*, 5816–5817; e) C. P. Casey, T. B. Clark, I. A. Guzei, *J. Am. Chem. Soc.* **2007**, *129*, 11821–11827; f) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2009**, *131*, 2499–2507.

[15] a) R. C. Linck, R. J. Pafford, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 8856–8857; b) J. S. M. Samec, J. E. Bäckvall, P.-G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; c) M. Ito, T. Ikariya, *Chem. Commun.* **2007**, 5134–5142; d) Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2007**, *129*, 14303–14310; e) M. Ito, A. Sakaguchi, C. Kobayashi, T. Ikariya, *J. Am. Chem. Soc.* **2007**, *129*, 290–291; f) M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788–789; g) Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2009**, *131*, 3593–3600.

[16] W. Kaim, *Inorg. Chem.* **2011**, *50*, DOI: 10.1021/ic2003832.

[17] W. I. Dzik, X. P. Zhang, B. de Bruin, *Inorg. Chem.* **2011**, *50*, DOI: 10.1021/ic200043a.

[18] a) C. S. Scarborough, K. Wieghardt, *Inorg. Chem.* **2011**, *50*, DOI: 10.1021/ic2005419; b) S. Sproules, K. Wieghardt, *Coord. Chem. Rev.* **2010**, *254*, 1358–1382; c) C. C. Lu, T. Weyhermüller, E. Bill, K. Wieghardt, *Inorg. Chem.* **2009**, *48*, 6055–6064; d) S. Sproules, K. Wieghardt, *Dalton Trans.* **2007**, 1552–1566.

[19] A. M. Allgeier, C. A. Mirkin, *Angew. Chem.* **1998**, *110*, 936; *Angew. Chem. Int. Ed.* **1998**, *37*, 894–908.

[20] K. Caulton, *Eur. J. Inorg. Chem.* **2012**, DOI: 10.1002/ejic.201100623.

[21] B. de Bruin, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936–2947. See also: a) V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745–1776; b) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox, M. van Meurs, *Angew. Chem.* **2002**, *114*, 507; *Angew. Chem. Int. Ed.* **2002**, *41*, 489–491; c) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2001**, *113*, 4855; *Angew. Chem. Int. Ed.* **2001**, *40*, 4719–4722; d) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P.

White, D. J. Williams, *Chem. Commun.* **1998**, 849–850; e) B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050.

[22] a) W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin, *Angew. Chem. Int. Ed.* **2011**, *50*, 3356–3358; b) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794–795.

[23] a) S. K. Russell, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, *133*, 8858–8861; b) S. K. Russell, C. Milsmann, E. Lobkovsky, T. Weyhermüller, P. J. Chirik, *Inorg. Chem.* **2011**, *50*, 3159–3169; c) A. M. Tondreau, C. Milsmann, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2011**, *50*, doi: 10.1021/ic200730k; d) S. K. Russell, J. M. Darmon, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2010**, *49*, 2782–2792; e) K. T. Sylvester, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8777–8779.

[24] M. M. P. Grutters, J. I. van der Vlugt, Y. Pei, A. M. Mills, M. Lutz, A. L. Spek, C. Müller, C. Moberg, D. Vogt, *Adv. Synth. Catal.* **2009**, *351*, 2199–2208. See also: M. M. P. Grutters, C. Müller, D. Vogt, *J. Am. Chem. Soc.* **2006**, *128*, 7414–7415.

[25] a) A. M. Tondreau, C. Milsmann, A. D. Patrick, H. M. Hoyt, E. Lobkovsky, J. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 15046–15059; b) B. M. Wile, R. J. Trovitch, S. C. Bart, A. M. Tondreau, E. Lobkovsky, C. Milsmann, E. Bill, K. Wieghardt, P. J. Chirik, *Inorg. Chem.* **2009**, *48*, 4190–4200; c) A. C. Bowman, S. C. Bart, F. W. Heinemann, K. Meyer, P. J. Chirik, *Inorg. Chem.* **2009**, *48*, 5587; d) S. K. Russell, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 36; e) R. J. Trovitch, E. Lobkovsky, M. W. Bouwkamp, P. J. Chirik, *Organometallics* **2008**, *27*, 6264–6278; f) R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 11631–11640; g) M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13340–13341; h) M. W. Bouwkamp, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2006**, *45*, 2–4.

[26] A. L. Smith, K. I. Hardcastle, J. D. Soper, *J. Am. Chem. Soc.* **2010**, *132*, 14358. See also: A. L. Smith, L. A. Clapp, K. I. Hardcastle, J. D. Soper, *Polyhedron* **2010**, *29*, 164–169.

[27] D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Meyer, D. J. Mindiola, *J. Am. Chem. Soc.* **2008**, *130*, 3676–3682.

[28] a) J. C. Peters, S. B. Harkins, S. D. Brown, M. W. Day, *Inorg. Chem.* **2001**, *40*, 5083–5091; b) S. B. Harkins, J. C. Peters, *Organometallics* **2002**, *21*, 1753–1755; c) S. B. Harkins, J. C. Peters, *Inorg. Chem.* **2006**, *45*, 4316–4318; d) T. A. Betley, B. A. Qian, J. C. Peters, *Inorg. Chem.* **2008**, *47*, 11570–11582; e) D. L. M. Suess, J. C. Peters, *Chem. Commun.* **2010**, *46*, 6554–6556.

[29] a) O. Vechorkin, V. Proust, X. Hu, *J. Am. Chem. Soc.* **2009**, *131*, 9756–9766; b) O. Vechorkin, Z. Csok, R. Scopelliti, X. Hu, *Chem. Eur. J.* **2009**, *15*, 3889–3999.

[30] P. Ren, O. Vechorkin, K. von Allmen, R. Scopelliti, X. Hu, *J. Am. Chem. Soc.* **2011**, *133*, 7084–7095.

[31] For a recent review on catalytic C–H activation using metalloporphyrins, see: H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899–1909. For other reviews on metal-carbenoid based C–H functionalization, see: a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; b) C. J. Moody, *Angew. Chem. Int. Ed.* **2007**, *46*, 9148–9150; c) M. P. Doyle, *Angew. Chem.* **2009**, *121*, 864; *Angew. Chem. Int. Ed.* **2009**, *48*, 850–852; d) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704–724; e) H. M. L. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857–1869.

[32] a) Y. Chen, K. B. Fields, X. P. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719; b) Y. Chen, J. V. Ruppel, X. P. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 12074–12075; c) S. Zhu, J. V. Ruppel, H. Lu, L. Wojtas, X. P. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043.

[33] a) W. I. Dzik, X. Xu, X. P. Zhang, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902; b) H. J. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin, X. P. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521.

[34] a) A. I. Olivos-Suarez, H. Jiang, X. P. Zhang, B. de Bruin, *Dalton Trans.* **2011**, *40*, 5697–5705; b) V. Lyaskovskyy, A. I. Olivos-Suarez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264–12273.

[35] A. D. Pryde, B. L. Shaw, B. Weeks, *J. Chem. Soc., Dalton Trans.* **1976**, 322–327.

[36] For general reviews, see: a) M. T. Whited, R. H. Grubbs, *Acc. Chem. Res.* **2009**, *42*, 1607–1616; b) D. Morales-Morales, C. M. Jensen, in *the Chemistry of Pincer Compounds*, Elsevier, Amsterdam, **2007**; c) L.-C. Liang, *Coord. Chem. Rev.* **2006**, *250*, 1152–1177; d) M. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792.

[37] a) J. I. van der Vlugt, *Angew. Chem. Int. Ed.* **2010**, *49*, 252–255; b) Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201–9203; c) A. M. Spokoyny, M. G. Reuter, C. L. Stern, M. A. Ratner, T. Seideman, C. A. Mirkin, *J. Am. Chem. Soc.* **2009**, *131*, 9482–9483.

[38] a) D. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner, M. Pollak, K. Mereiter, J. Kisala, K. Kirchner, *Organometallics* **2006**, *25*, 1900–1913; b) D. Benito-Garagorri, K. Kirchner, *Acc. Chem. Res.* **2008**, *41*, 201–213; c) W. Schirmer, U. Flörke, H.-J. Haupt, *Z. Anorg. Allg. Chem.* **1987**, *545*, 83–97.

[39] a) W. H. Bernskoetter, S. Kloek Hanson, S. K. Buzak, Z. Davis, P. S. White, R. Swartz, K. I. Goldberg, M. Brookhart, *J. Am. Chem. Soc.* **2009**, *131*, 8603–8613; b) H. Salem, L. J. W. Shimon, Y. Diskin-Posner, G. Leitus, Y. Ben-David, D. Milstein, *Organometallics* **2009**, *28*, 4791–4806.

[40] J. I. van der Vlugt, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 8990; *Angew. Chem. Int. Ed.* **2009**, *48*, 8832–8846.

[41] a) B. Askervold, J. Torres Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen, S. Schneider, *Nature Chem.* **2011**, *3*, 532–537; b) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem. Int. Ed.* **2011**, *50*, 3533–3537; c) K. Muñiz, A. Lishchynskyi, J. Streuff, M. Nieger, E. C. Escudero-Adán, M. Martínez Belmonte, *Chem. Commun.* **2011**, *47*, 4911–4913; d) N. Nebra, N. Saffon, L. Maron, B. Martin-Vaca, D. Bourissou, *Inorg. Chem.* **2011**, *50*, 6378–6383; e) N. Nebra, J. Lisena, N. Saffon, L. Maron, B. Martin-Vaca, D. Bourissou, *Dalton Trans.* **2011**, *40*, 8912–8921; f) N. Tsoureas, Y.-Y. Kuo, M. F. Haddow, G. R. Owen, *Chem. Commun.* **2011**, *46*, 484–486; g) P. Oulie, N. Nebra, N. Saffon, L. Maron, B. Martin-Vaca, D. Bourissou, *J. Am. Chem. Soc.* **2009**, *131*, 3493–3498.

[42] J. Zhang, M. Gandelman, D. Herrman, G. Leitus, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Inorg. Chim. Acta* **2006**, *359*, 1955–1960.

[43] E. M. Pelczar, T. J. Emge, K. Krogh-Jespersen, A. S. Goldman, *Organometallics* **2008**, *27*, 5759–5767.

[44] R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2006**, *45*, 7252–7260.

[45] a) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2011**, *50*, 2120–2124; comprehensive highlight: b) G. Bauer, K. A. Kirchner, *Angew. Chem. Int. Ed.* **2011**, *50*, 5798–5800.

[46] R. M. Bullock, *Catalysis without Precious Metals*, Wiley-VCH, Weinheim, Germany, **2010**. See also: a) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511; b) B. Plietker, *Iron Catalysis in Organic Synthesis; Reactions and Applications*, **2008**, Wiley-VCH; c) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730–2744.

[47] a) J. I. van der Vlugt, M. Lutz, E. A. Pidko, D. Vogt, A. L. Spek, *Dalton Trans.* **2009**, 1016–1023; b) M. Lutz, J. I. van der Vlugt, D. Vogt, A. L. Spek, *Polyhedron* **2009**, *28*, 2341–2346.

[48] J. I. van der Vlugt, E. A. Pidko, D. Vogt, M. Lutz, A. L. Spek, A. Meetsma, *Inorg. Chem.* **2008**, *47*, 4442–4444.

[49] J. I. van der Vlugt, E. A. Pidko, D. Vogt, M. Lutz, A. L. Spek, *Inorg. Chem.* **2009**, *48*, 7513–7515.

[50] J. I. van der Vlugt, E. A. Pidko, R. C. Bauer, Y. Gloaguen, M. K. Rong, M. Lutz, *Chem. Eur. J.* **2011**, *17*, 3850–3854.

[51] S. Y. de Boer, Y. Gloaguen, M. Lutz, J. I. van der Vlugt, *Inorg. Chim. Acta* **2011**; DOI: 10.1016/j.ica.2011.10.037.

[52] The classic Shvo-catalyst is another landmark example of co-operative catalysis with Ru, see ref. [14] and: 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; c) T. C. Johnson, G. H. Clarkson, M. Wills, *Organometallics* **2011**, *30*, 1859–1868; d) H. Zhang, D. Chen, Y. Zhang, G. Zhang, J. Liu, *Dalton Trans.* **2010**, *39*, 1972–1978.

[53] a) U. J. Kilgore, J. A. S. Roberts, D. H. Pool, A. M. Appel, M. P. Stewart, M. Rakowski DuBois, W. G. Dougherty, W. S. Kassel, R. M. Bullock, D. L. DuBois, *J. Am. Chem. Soc.* **2011**, *133*, 5861–5872; b) D. L. DuBois, R. M. Bullock, *Eur. J. Inorg. Chem.* **2011**, 1017–1027; c) M. Rakowski DuBois, D. L. DuBois, in: *Catalysis without Precious Metals* (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, Germany, **2010**, p. 165–180; d) E. S. Wiedner, J. Y. Yang, W. G. Dougherty, W. S. Kassel, R. M. Bullock, M. Rakowski DuBois, D. L. DuBois, *Organometallics* **2010**, *29*, 5390–5401; e) M. Rakowski DuBois, D. L. DuBois, *Acc. Chem. Res.* **2009**, *42*, 1974–1982; f) M. Rakowski DuBois, D. L. DuBois, *Chem. Soc. Rev.* **2009**, *38*, 62–72; g) G. M. Jacobsen, J. Y. Yang, B. Twamley, A. D. Wilson, R. M. Bullock, M. Rakowski DuBois, D. L. DuBois, *Energy Environ. Sci.* **2008**, *1*, 167–174; h) M. Rakowski DuBois, D. L. DuBois, *C. R. Chim.* **2008**, *11*, 805–817.

[54] A. Le Goff, V. Artero, B. Jousselme, P. D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave, *Science* **2009**, *326*, 1384–1387.

[55] P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave, V. Artero, *Angew. Chem. Int. Ed.* **2011**, *50*, 1371–1374.

[56] M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, *Chem. Commun.* **2011**, *47*, 7989–7991.

[57] a) S. Ezzaher, J.-F. Capon, F. Gloaguen, F. Pétillon, P. Schollhammer, J. Talarmin, N. Kervarec, *Inorg. Chem.* **2009**, *48*, 2–4; see also: b) N. Wang, M. Wang, T. Zhang, P. Li, J. Liua, L. Sun, *Chem. Commun.* **2008**, 5800–5802; c) N. Wang, M. Wang, T. Zhang, P. Li, J. Liua, L. Sun, *Inorg. Chem.* **2009**, *48*, 11551–11558.

[58] S. Kaur-Ghumaan, L. Schwartz, R. Lomoth, M. Stein, S. Ott, *Angew. Chem. Int. Ed.* **2010**, *49*, 8033–8036.

[59] R. D. Adams, F. A. Cotton, *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, Wiley-VCH, New York, **1998**.

[60] For a recent review, see: M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141–163. See also: M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019.

[61] a) R. G. Konsler, J. Karl, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 10780–10781; b) R. Breinbauer, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2000**, *39*, 3640–3607.

[62] a) R. M. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 2713–2723; b) R. M. Haak, M. Martínez Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans.* **2010**, *39*, 593–602.

[63] a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; b) M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952–3015; c) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302–1315; d) L. Liang, D. Astruc, *Coord. Chem. Rev.* **2011**, DOI:10.1016/j.ccr.2011.06.028.

[64] B. A. Rodriguez, M. Delferro, T. J. Marks, *J. Am. Chem. Soc.* **2009**, *131*, 5902–5919.

[65] For a general review, see: J. Klingele, S. Dechert, F. Meyer, *Coord. Chem. Rev.* **2009**, *253*, 2698–2741. For specific examples for Ni, see: a) T. Graef, J. Galezowska, S. Dechert, F. Meyer, *Eur. J. Inorg. Chem.* **2011**, 4161–4167; b) A. Sachse, S. Demeshko, S. Dechert, V. Daebel, A. Lange, F. Meyer, *Dalton Trans.* **2010**, *39*, 3903–3914; c) S. V. Kryatov, E. V. Rybak-Akimova, F. Meyer, H. Pritzkow, *Eur. J. Inorg. Chem.* **2003**, 1581–1590.

[66] a) M. Jarenmark, E. Csapó, J. Singh, S. Wöckel, E. Farkas, F. Meyer, M. Haukka, E. Nordlander, *Dalton Trans.* **2010**, *39*,

8183–8194; b) M. Jarenmark, M. Haukka, S. Demeshko, F. Tuczek, L. Zuppiroli, F. Meyer, E. Nordlander, *Inorg. Chem.* **2011**, *50*, 3866–3887; c) L. V. Penkova, A. Maciag, E. V. Rybak-Akimova, M. Haukka, V. A. Pavlenko, T. S. Iskenderov, H. Kozlowski, F. Meyer, I. O. Fritzky, *Inorg. Chem.* **2009**, *48*, 6960–6971; d) B. Bauer-Siebenlist, S. Dechert, F. Meyer, *Chem. Eur. J.* **2005**, *11*, 5343–5352; e) B. Bauer-Siebenlist, F. Meyer, E. Farkas, D. Vidovic, S. Dechert, F. Meyer, *Chem. Eur. J.* **2005**, *11*, 4349–4360; f) B. Bauer-Siebenlist, F. Meyer, E. Farkas, D. Vidovic, J. A. C. Seijo, R. Herbst-Irmer, H. Pritzkow, *Inorg. Chem.* **2004**, *43*, 4189–4202.

[67] a) A. Prokofieva, S. Dechert, C. Grosse, G. M. Sheldrick, F. Meyer, *Chem. Eur. J.* **2009**, *15*, 4994–4997; b) A. Prokofieva, A. I. Prikhod'ko, S. Dechert, F. Meyer, *Chem. Commun.* **2008**, 1005–1007; c) J. Ackermann, S. Buchler, F. Meyer, *C. R. Chim.* **2007**, *10*, 421–432; d) J. Ackermann, F. Meyer, E. Kaifer, H. Pritzkow, *Chem. Eur. J.* **2002**, *8*, 247–258.

[68] For other Cu-systems with dinucleating pyrazolate ligands, see: a) M. Stollenz, H. Gehring, V. Konstanzer, S. Fischer, S. Dechert, C. Grosse, F. Meyer, *Organometallics* **2011**, *31*, 3708–3725; b) A. K. Singh, J. I. van der Vlugt, S. Demeshko, S. Dechert, F. Meyer, *Eur. J. Inorg. Chem.* **2009**, 3431–3439; c) J. I. van der Vlugt, S. Demeshko, S. Dechert, F. Meyer, *Inorg. Chem.* **2008**, *47*, 1576–1585; d) M. Stollenz, C. Grosse, F. Meyer, *Chem. Commun.* **2008**, 1744–1746.

[69] C. M. Fafard, D. Adhikari, B. M. Foxman, D. J. Mindiola, O. V. Ozerov, *J. Am. Chem. Soc.* **2007**, *129*, 10318–10319.

[70] a) S. B. Harkins, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 2885–2893; b) S. B. Harkins, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 2030–2031; c) N. P. Mankad, E. Rivard, S. B. Harkins, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 16032–16033; d) S. B. Harkins, N. P. Mankad, A. J. M. Miller, R. K. Szilagyi, J. C. Peters, *J. Am. Chem. Soc.* **2008**, *130*, 3478–3485; e) J. C. Deaton, S. C. Switalski, D. Y. Kondakov, R. H. Young, T. D. Pawlik, D. J. Giesen, S. B. Harkins, A. J. M. Miller, S. F. Mickenberg, J. C. Peters, *J. Am. Chem. Soc.* **2010**, *132*, 9499–9508.

[71] For other applications of this PPP-scaffold with second- and third-row metals, see: a) M. Mazzeo, M. Lamberti, A. Massa, A. Scettri, C. Pellecchia, J. C. Peters, *Organometallics* **2008**, *27*, 5741; b) M. Mazzeo, M. Lamberti, I. d'Auria, S. Milione, J. C. Peters, C. Pellecchia, *J. Polym. Sci. Polym. Chem. Ed.* **2010**, *48*, 1374; c) M. Mazzeo, M. Strianese, O. Kühl, J. C. Peters, *Dalton Trans.* **2011**, *40*, 9026–9033.

[72] R. C. Bauer, Y. Gloaguen, M. Lutz, J. N. H. Reek, B. de Bruin, J. I. van der Vlugt, *Dalton Trans.* **2011**, *40*, 8822–8829.

[73] A. R. Fout, F. Bauli, H. Fan, J. Tomaszewski, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *Angew. Chem.* **2006**, *118*, 3369; *Angew. Chem. Int. Ed.* **2006**, *45*, 3291–3295.

[74] a) U. Christmann, R. Vilar, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 1294–1295; b) U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras, R. Vilar, *J. Am. Chem. Soc.* **2006**, *128*, 6376–390.

[75] a) A. Velian, S. Lin, A. J. M. Miller, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297; b) S. Lin, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2011**, *133*, 3828–3831; c) S. T. Chao, N. C. Lara, S. Lin, M. W. Day, T. Agapie, *Angew. Chem. Int. Ed.* **2011**, *50*, 7529–7532. For related terphenyl-based diphosphanes, see: J. I. van der Vlugt, R. van Duren, G. D. Batema, R. den Heeten, A. Meetsma, J. Fraanje, K. Goubitz, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Organometallics* **2005**, *24*, 5377–5382.

[76] a) C. A. Laskowski, G. L. Hillhouse, *Chem. Sci.* **2011**, *2*, 321–325; b) R. Beck, S. A. Johnson, *Chem. Commun.* **2011**, *47*, 9233–9235.

[77] For reviews on the use of C_3-symmetric systems in catalysis, see: a) C. Moberg, *Angew. Chem.* **1998**, *110*, 260; *Angew. Chem. Int. Ed.* **1998**, *37*, 248–268; b) S. E. Gibson, M. P. Castaldi, *Chem. Commun.* **2006**, 3045–3062; see also: c) J. Wassenaar, M. A. Siegler, A. L. Spek, B. de Bruin, J. N. H. Reek, J. I. van der Vlugt, *Inorg. Chem.* **2010**, *49*, 6495–6508; d) M. M. P.

Grutters, J. I. van der Vlugt, Y. Pei, A. M. Mills, M. Lutz, A. L. Spek, C. Müller, C. Moberg, D. Vogt, *Adv. Synth. Catal.* **2009**, *351*, 2199–2208; e) M. Ciclosi, J. Lloret, F. Estevan, P. Lauerta, M. Sanaú, J. Pérez-Prieto, *Angew. Chem.* **2006**, *118*, 6893; *Angew. Chem. Int. Ed.* **2006**, *45*, 6741–6744; f) G. Ionescu, J. I. van der Vlugt, H. C. L. Abbenhuis, D. Vogt, *Tetrahedron: Asymmetry* **2005**, *16*, 3970–3975; g) J. I. van der Vlugt, M. M. P. Grutters, J. Ackerstaff, R. W. J. M. Hanssen, H. C. L. Abbenhuis, D. Vogt, *Tetrahedron Lett.* **2003**, *44*, 8301–8305.

[78] a) Q. Zhao, T. A. Betley, *Angew. Chem. Int. Ed.* **2011**, *50*, 709–712; b) T. M. Powers, A. R. Fout, S.-L. Zheng, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 3336–3338; c) Q. Zhao, T. D. Harris, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 8293–8306; d) T. D. Harris, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, doi: 10.1021/ja2052655.

[79] This approach of mimicking heterogeneous catalysts using homogeneous model systems is reminiscent of the modeling of silica surfaces using silsesquioxane frameworks, see: a) R. Duchateau, *Chem. Rev.* **2002**, *102*, 3525–3542; b) J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073–4147; see also: c) J. I. van der Vlugt, J. Ackerstaff, T. W. Dijkstra, A. M. Mills, H. Kooijman, A. L. Spek, A. Meetsma, H. C. L. Abbenhuis, D. Vogt, *Adv. Synth. Catal.* **2004**, *346*, 399–412; d) J. I. van der Vlugt, M. Fioroni, J. Ackerstaff, R. W. J. M. Hanssen, A. M. Mills, A. L. Spek, A. Meetsma, H. C. L. Abbenhuis, D. Vogt, *Organometallics* **2003**, *22*, 5297–5306; e) H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25–32.

[80] a) E. Y. Tsui, M. W. Day, T. Agapie, *Angew. Chem. Int. Ed.* **2011**, *50*, 1668–1672; b) E. Y. Tsui, J. S. Kanady, M. W. Day, T. Agapie, *Chem. Commun.* **2011**, *47*, 4189–4191. See also: J. S. Kanady, E. Y. Tsui, M. W. Day, T. Agapie, *Science* **2011**, *333*, 733–736.

[81] R. Angamuthu, P. Byers, M. Lutz, A. L. Spek, E. Bouwman, *Science* **2010**, *327*, 313–315.

[82] J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658. This paper described the first hemilabile coordination of (*o*-diphenylphosphanyl)anisole. For related bisphosphanes with this motif, see: a) J. I. van der Vlugt, J. M. Bonet, A. M. Mills, A. L. Spek, D. Vogt, *Tetrahedron Lett.* **2003**, *44*, 4389–4392; b) J. I. van der Vlugt, M. M. P. Grutters, A. M. Mills, H. Kooijman, A. L. Spek, D. Vogt, *Eur. J. Inorg. Chem.* **2003**, 4361–4369.

[83] a) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702; *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699; b) P. Braunstein, *J. Organomet. Chem.* **2004**, *689*, 3953–3967; c) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233; d) G. W. Parshall, S. D. Ittel, in: *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed., Wiley-Interscience, New York, **1992**, pp. 70; e) W. Keim, *Angew. Chem.* **1990**, *102*, 251; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244.

[84] a) M. J. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2011**, *50*, 114–137; b) H. Jae Yoon, C. A. Mirkin, *J. Am. Chem. Soc.* **2008**, *130*, 11590–11591; c) C. G. Oliveri, P. I. A. Ulmann, M. J. Wiester, C. A. Mirkin, *Acc. Chem. Res.* **2008**, *41*, 1618–1629; d) H. J. Yoon, J. Heo, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 14182–14183; e) M. S. Masar III, N. C. Gianneschi, C. G. Oliveri, C. L. Stern, S. T. Nguyen, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 10149–10158.

[85] H. J. Yoon, J. Kuwabara, J.-H. Kim, C. A. Mirkin, *Science* **2010**, *330*, 66–69.

[86] C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602.

[87] R. Lindner, B. van den Bosch, M. Lutz, J. N. H. Reek, J. I. van der Vlugt, *Organometallics* **2011**, *30*, 499–510. For related examples of such hybrid PNN-ligands (but without studies on their hemilabile character), see: a) N. G. Leonard, P. G. Williard, W. H. Bernskoetter, *Dalton Trans.* **2011**, *40*, 4300–4306; b) A. Choualeb, A. J. Lough, D. G. Gusev, *Organometallics* **2007**, *26*, 5224–5229; c) W.-Y. Lee, L.-C. Liang, *Dalton Trans.* **2005**, 1952–1956.

[88] a) J. I. van der Vlugt, J. N. H. Reek, in: *Phosphorus Ligands: Design and Synthesis* (Eds.: P. C. J. Kamer, P. W. N. M. van Leeuwen), Wiley-VCH, Weinheim, Germany, **2011**, in press; b) F. W. Patureau, S. de Boer, P.-A. R. Breuil, J. Meeuwissen, M. A. Siegler, A. L. Spek, A. J. Sandee, B. de Bruin, *J. N. H. Reek, J. Am. Chem. Soc.* **2009**, *131*, 6683–6685.

[89] General reviews introducing the area: a) W. Seiche, B. Breit, in: *Phosphorus Ligands in Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, Germany, **2008**, p. 1379–1404; b) B. Breit, in: *Supramolecular Catalysis* (Ed.: P. W. N. M. van Leeuwen), Wiley-VCH, Weinheim, Germany, **2008**, p. 29–56; c) J. N. H. Reek, in: *Supramolecular Catalysis* (Ed.: P. W. N. M. van Leeuwen), Wiley-VCH, Weinheim, Germany, **2008**, p. 199–234.

[90] a) A. S. Borovik, *Chem. Soc. Rev.* **2011**, *40*, 1870–1874; b) R. L. Shook, A. S. Borovik, *Chem. Commun.* **2008**, 6095–6107; c) R. L. Shook, S. M. Peterson, J. Greaves, C. Moore, A. L. Rheingold, A. S. Borovik, *J. Am. Chem. Soc.* **2011**, *133*, 5810–5817.

[91] M. de Greef, B. Breit, *Angew. Chem.* **2009**, *121*, 559; *Angew. Chem. Int. Ed.* **2009**, *48*, 551–554.

[92] J. Meeuwissen, J. N. H. Reek, *Nature Chem.* **2010**, *2*, 615–621.

[93] S. Das, C. D. Incarvito, R. H. Crabtree, G. W. Brudvig, *Science* **2006**, *312*, 1941–1943.

[94] a) J.-W. Park, J.-H. Park, C.-H. Jun, *J. Org. Chem.* **2008**, *73*, 5598–5601; b) J.-H. Park, J.-W. Park, C.-H. Jun, *Acc. Chem. Res.* **2008**, *41*, 222–234.

[95] a) N. R. Vautravers, D. D. Regent, B. Breit, *Chem. Commun.* **2011**, *47*, 6635–6637; b) T. Šmejkal, D. Gribkov, J. Geier, M. Keller, B. Breit, *Chem. Eur. J.* **2010**, *16*, 2470–2478; c) L. Diab, T. Šmejkal, J. Geier, B. Breit, *Angew. Chem.* **2009**, *121*, 8166; *Angew. Chem. Int. Ed.* **2009**, *48*, 8022–8026.

[96] P.-A. R. Breuil, F. W. Patureau, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 2196; *Angew. Chem. Int. Ed.* **2009**, *48*, 2162–2165.

[97] P. Dydio, W. I. Dzik, M. Lutz, B. de Bruin, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2011**, *50*, 396–400.

[98] NH_3: a) J. I. van der Vlugt, *Chem. Soc. Rev.* **2010**, *39*, 2302–2322; b) J. L. Klinkenberg, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 86–95; c) E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang, D. Milstein, *J. Am. Chem. Soc.* **2010**, *132*, 8542–8543.

[99] H_2: a) M. R. Ringenberg, S. Latha Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788–789; b) W. Cui, B. B. Wayland, *J. Am. Chem. Soc.* **2004**, *126*, 8266–8274; c) J. Wassenaar, B. de Bruin, M. A. Siegler, A. L. Spek, J. N. H. Reek, J. I. van der Vlugt, *Chem. Commun.* **2010**, *46*, 1232–1234.

[100] D. G. H. Hetterscheid, J. I. van der Vlugt, B. de Bruin, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 8324; *Angew. Chem. Int. Ed.* **2009**, *48*, 8178–818.