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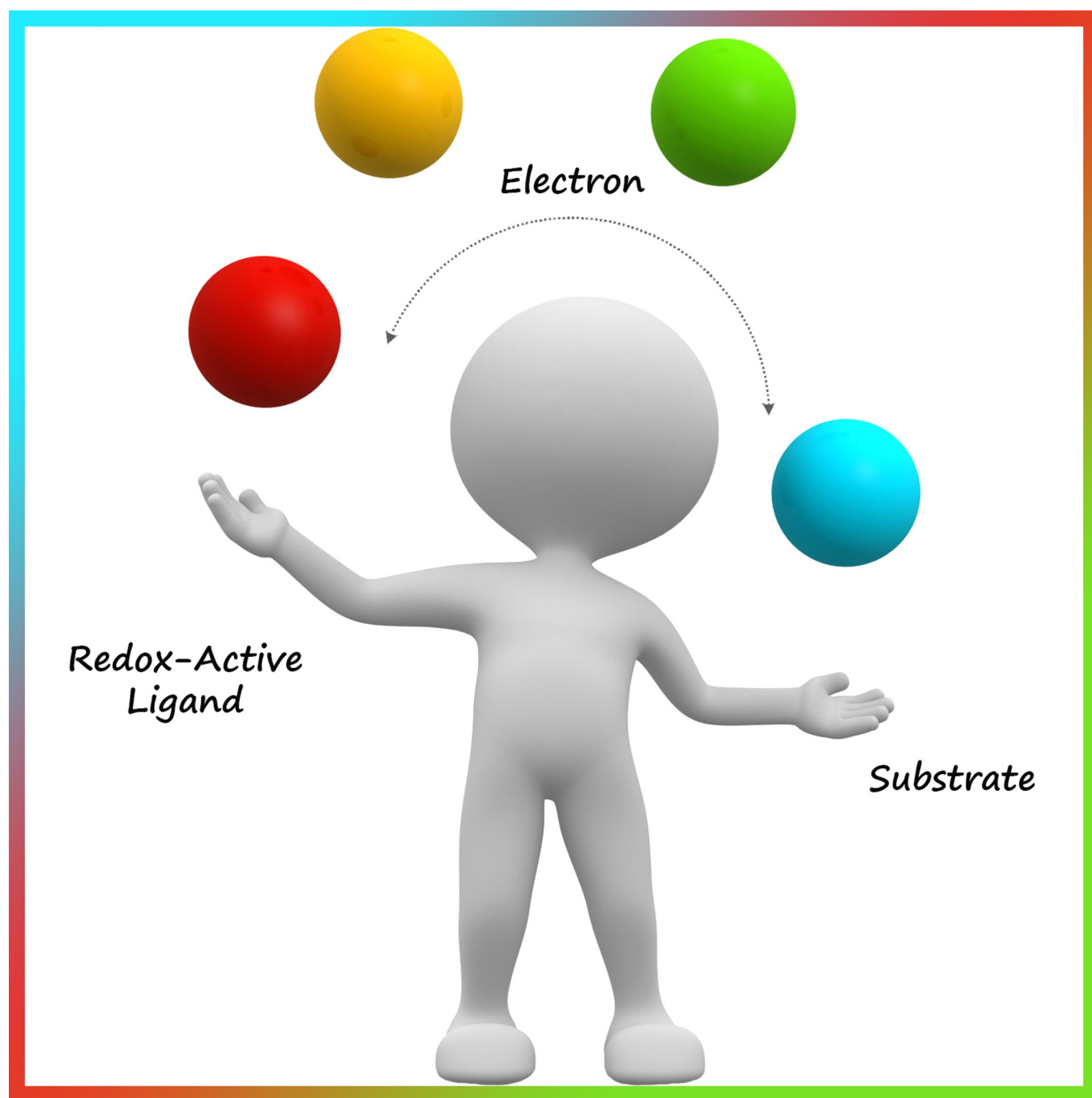
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Redox Catalysis

Radical-Type Reactivity and Catalysis by Single-Electron Transfer to or from Redox-Active Ligands

Jarl Ivar van der Vlugt^{*[a]}

Abstract: Controlled ligand-based redox-activity and chemical non-innocence are rapidly gaining importance for selective (catalytic) processes. This Concept aims to provide an overview of the progress regarding ligand-to-substrate single-electron transfer as a relatively new mode of operation to exploit ligand-centered reactivity and catalysis based thereon.

Introduction

Storing and releasing redox-equivalents (electrons) in non-innocent or reactive ligand scaffolds is becoming a very important and effective strategy in both catalysis and renewable fuel research. Shuttling of electrons can be achieved using so-called redox-active ligands, that is, organic fragments that can reversibly shuttle between at least two well-defined redox-states whilst bound to a metal(loid) center, the oxidation state of which does not need to be significantly affected by this transformation (Figure 1). In cases where a more ambiguous

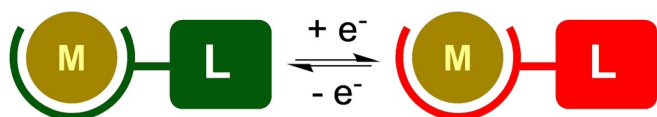


Figure 1. General depiction of reversible ligand centered redox process. Green = oxidized ligand; red = reduced ligand.

overall electronic structure ensues from strong electronic coupling between a ligand and a metal center, the term redox-noninnocence may be more appropriate.^[1] Well-known examples of redox-active ligands are dithiolenes,^[2] donor appended diarylamines,^[3] heterodienes such as 1,4-diimine and related 2-iminopyridines as well as bis(imino)pyridines,^[4] olefin-appended diazadienes,^[5] salens and derivatives thereof,^[3],6] and dipyrins as well as extended systems such as porphyrins.^[7] Newer additions have appeared as well, including verdazyl,^[8] and nindigo,^[9] formazanate,^[10] aminotropimate,^[11] arylazopyridine,^[12] π -coordinated arene and derivatives thereof,^[13] β -diketiminato^[14] and various others.^[15] Particularly well-studied are ligands bearing the redox-active 1,2-catechol or *o*-phenylenediamine^[16,17] moiety or the hybrid *o*-aminophenol^[18,19] fragment, which can bind to a metal center in three different oxidation

states: the two-electron reduced (dianionic), one-electron reduced/oxidized (monoanionic ligand radical) and two-electron oxidized form (neutral).

Modes of reactivity of redox-active ligands

Beyond the intriguing spectroscopic and magnetochemical features of redox-active ligands, which have been intense subject of research over the last decades recent developments have primarily focused on the possibilities for these platforms to accommodate and modulate chemical reactions at a bound transition metal. A major thrust for the use of redox-active ligands has been as electron reservoir for storing and releasing redox equivalents that may be generated or required at a metal center during substrate activation.^[20] However, these ligand systems have been shown to also allow at least four other modes of operation, although each of these still need to be further explored to establish and exploit their full potential. Three of these modes are primarily related to the redox-active nature of these ligand platforms: i) tuning of the Lewis acidity or basicity of a transition metal by changing the ligand redox-state,^[21] ii) substrate activation by formation of a new ligand-substrate bond via radical reactivity^[22] and iii) metal–ligand bifunctional substrate activation by a one (ligand) plus one (metal), overall two-electron transfer^[23] (Figure 2). The fourth mode of operation (not displayed) relates to the potential chemical non-innocent nature of these platforms in terms of reversible (de)protonation and proton-shuttling abilities, which could allow for additional applications of redox-active ligands for metal-ligand bifunctional substrate activation.

Emerging strategies for radical catalysis

Several strategies for single-electron transfer-induced catalysis (e.g. photoredox catalysis, electron catalysis) have been developed, but although transition metals are sometimes involved as oxidant or reductant, many strategies result in the formation of (low concentrations of) free organic radicals. This may pose challenges with respect to, for example, chemoselectivity due to the highly reactive nature of many radical species.^[24,25] Metal-mediated atom transfer may afford more control, direct the reactivity of single-electron activated substrates and thereby provide alternatives to free radical strategies in terms of for example, chemoselectivity and substrate scope.^[26] In extremis, radical-type substrate species can be incorporated in the coordination sphere of a transition metal. One approach is metal-ligand radical-based catalysis using paramagnetic complexes based on a (transition) metal ion with only one unpaired electron ($S=1/2$), which allows for an electronic configuration wherein this unpaired electron can be transferred to an empty (acceptor) orbital at a bound substrate.^[27] This results in formal one-electron redox-events at both the metal ($M^{n+/(n+1)+}$) and substrate site. Only relatively few redox-active metals (e.g. Ti^{III} , Fe^{II} , Co^{II} , Rh^{II} , Cu^{II}) are available to facilitate the desired one-electron transfer using this strategy because the reduced and oxidized form of the redox-couple should be reversibly accessible and properly stabilized by the same ligand set.^[28]

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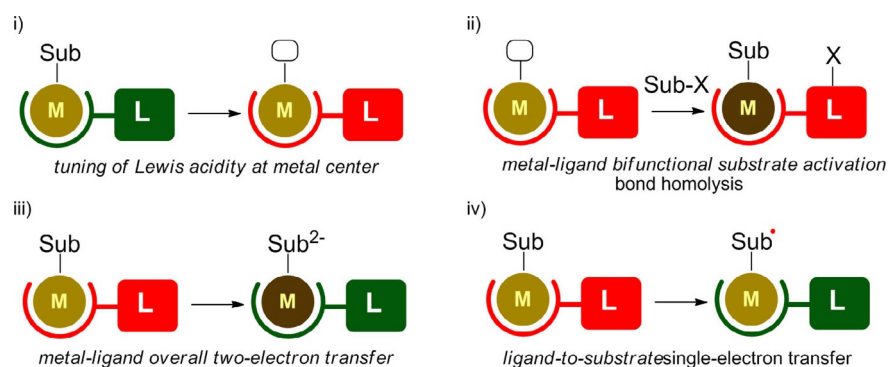


Figure 2. General depiction of three “established” modes (i–iii) of redox-active ligand reactivity that go beyond two-electron transfer to a metal center, as well as the new fourth mode (iv), highlighted in this Concept. Red = reduced ligand; green = oxidized ligand; light brown = metal in low oxidation state; dark brown = metal in high oxidation state.

An appealing alternative for metalloradical based catalysis would be to separate the locus of the redox-chemistry from the metal-centered substrate-binding event, harnessing the ligand redox-activity as one-electron reservoir to facilitate single-electron transfer with a substrate (Figure 2iv). This relatively new mode of ligand reactivity in synthetic chemistry and catalysis is the focus of this Concept. This type of ligand-centered redox-chemistry also finds resonance in a number of biological metalloenzyme systems such as horseradish peroxidase,^[29] intradiol catechol dioxygenase,^[30] galactose oxidase^[31] and cytochrome P450 that operate through mechanisms in which a redox-active ligand (e.g., a heme porphyrin, tyrosine-based phenolate or a thiolate) shuttles a single electron to (or from) a substrate.^[32]

The intrinsic differences between ligand-centered single-electron transfer and metalloradical-based reactivity are outlined in Figure 3. In the ligand centered strategy, the need for a redox-active metal is circumvented, allowing for more expanded coordination chemistry including noble, base and main-group metals, thus offering a wider palette with respect to substrate binding and pre-activation. Furthermore, there is more extensive opportunities to fine-tune the redox-properties of the ligand system by synthetic design (including strategies to extend to multinuclear architectures), and thus to potentially achieve control over the desirable redox-processes.

Stoichiometric Ligand-to-Substrate Single-Electron Transfer

The group of Soper reported that *cis*-Re^V(O)(Cl) precursor **A** bearing one amidophenolate ligand and a one-electron oxidized ligand L^{15Q} radical (i.e., a ligand mixed-valent system) interacts with half an equivalent of triphenylmethyl radical (Ph₃C·; Gomberg’s reagent) to give triphenylmethanol (Ph₃COH) and two new rhenium complexes, that is, a dichlorido-species **B** and oxo-bridged dimer **C** (Scheme 1, top).^[33] This outcome suggests that even on a coordinatively saturated metal center, the oxo ligands can be transformed into a reactive substrate. The atom-transfer reaction was suggested to occur by mixing of a populated Re=O π -bond with the ligand-centered L^{15Q} radical, which puts substantial spin density into the oxo oxygen atom (de facto creating an oxyl fragment), enabling the low-barrier radical coupling with the external organic radical, although computational studies were not performed to substantiate this proposal. Closed-shell oxorhenium homologues were found to be inert to Ph₃C·, suggesting at least some role for the ligand radical to activate the oxo-fragment during this transformation. The accompanying Re-complexes were suggested to result from disproportionation of the Re-species that are formed after O-atom transfer. The origin of the H atom in the formed alcohol product is unknown.

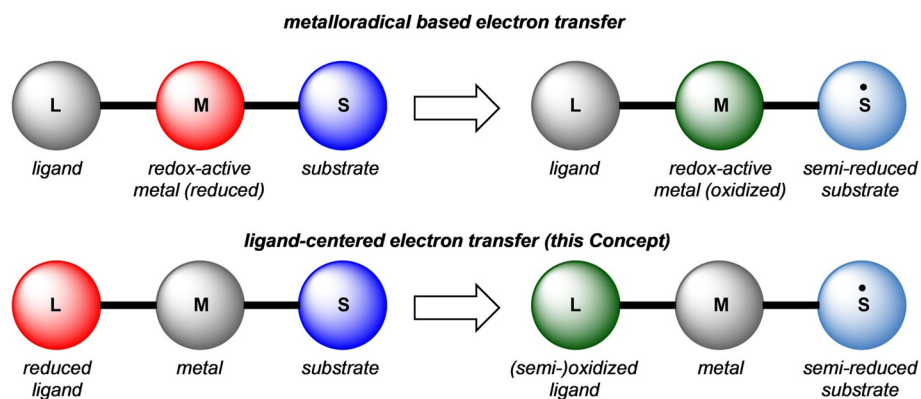
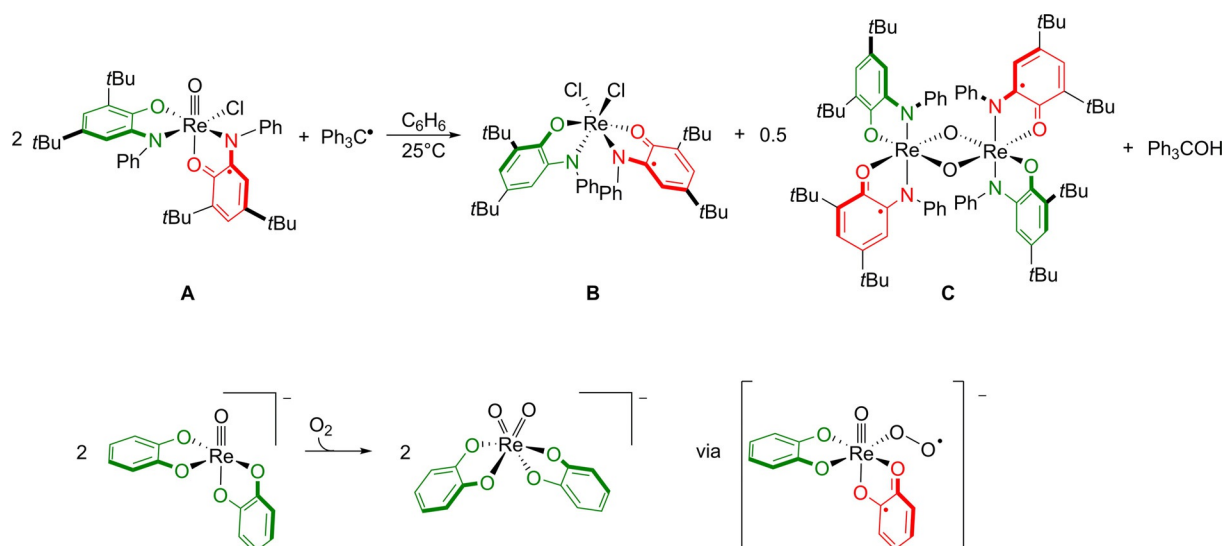


Figure 3. Metalloradical based vs. ligand-centered single-electron transfer reactivity. Red = reduced; green = oxidized (either metal or ligand).

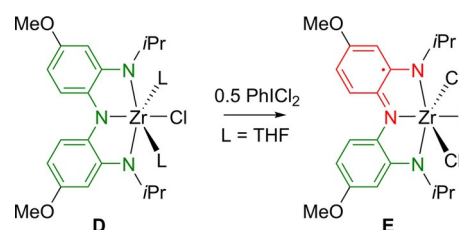


Scheme 1. Top: Oxygen atom transfer reaction of **A** with $\text{Ph}_3\text{C}^\bullet$ to produce Ph_3COH and two rhenium complexes **B** and **C**. Bottom: Homolysis of O_2 on bis(catecholate) derivative of **A** to give Re^{V} -dioxo derivative.

Soper and co-workers also demonstrated that the related Re^{V} -oxo complex bearing either two 2,4-di-*tert*-6-(phenylamido)phenolate ligands or two catecholate ligands allowed for the overall homolysis of O_2 (Scheme 1, bottom).^[34] A combined kinetic and computational study led to the proposition that upon coordination of O_2 , single-electron transfer from one of the redox-active ligands generates a superoxide species rhenium(V)(O_2^-), circumventing the rare formal Re^{VI} oxidation state and creating a ligand mixed-valent Re-species. The accompanying spin density delocalization aids in lowering the activation barrier for the formally spin-forbidden reaction between Re^{V} and dioxygen by allowing spin-crossover. Coupling with a second equivalent of the starting Re^{V} -oxo species leads to a μ -peroxy dinuclear intermediate from which the final Re^{VII} -bis(oxo)-product forms by O–O cleavage, with concomitant electron transfer back into the previously oxidized redox-active ligand. Control experiments with redox-inactive oxalate ligands gave no reaction, which is a strong indication of a crucial role for the ligand in this overall transformation. N–O cleavage in the stable nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO \cdot) was also possible using the same strategy.^[35]

Although formally not a direct ligand-to-substrate single electron transfer, Heyduk and co-workers demonstrated redox-active ligand-centered one-electron oxidation to facilitate the addition of a chlorine atom (Cl^\bullet) on a d^0 Zr^{IV} metal center in complex **D**, $\text{ZrCl}(\text{THF})_2(\text{L})$, by reaction with 0.5 molar equivalents of the two-electron oxidant PhICl_2 .^[36] This reaction yielded the paramagnetic $S = 1/2$ complex **E** $\text{ZrCl}_2(\text{THF})(\text{L}^\bullet)$, with the 1,2-diaminobenzene-derived tridentate trisanionic NNN ligand present as the one-electron oxidized ligand-centered radical L^\bullet (Scheme 2).

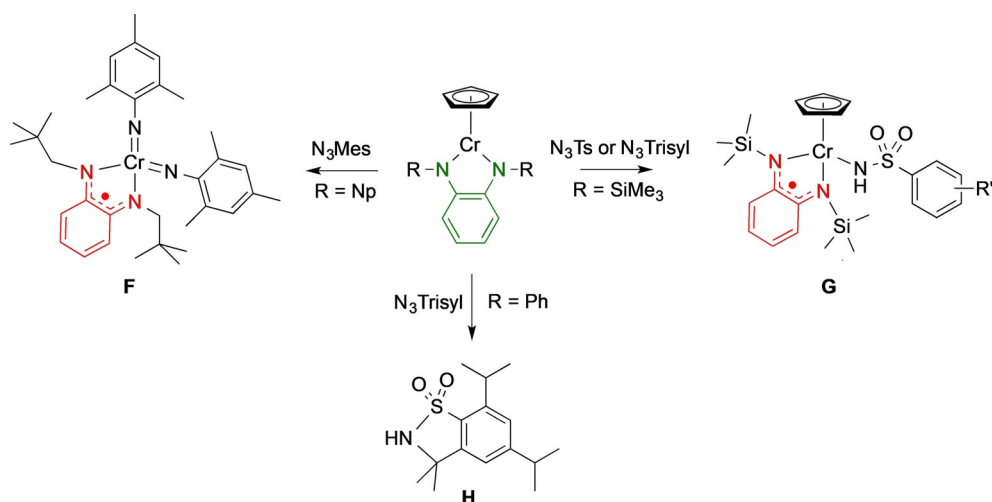
Smith and co-workers have reported the reactivity of coordinatively unsaturated $\text{Cr}^{\text{III}}(\text{Cp})$ complexes, bearing a range of redox-active diphenylamido NN ligands, towards organoazide substrates, with the outcome depending on both the substitution pattern of the azide reagent and the diamido ligand



Scheme 2. Ligand-facilitated single-electron oxidation on a $\text{Zr}^{\text{IV}}(\text{NNN})$ complex.

(Scheme 3).^[37] In selected cases, ligand-to-substrate single-electron transfer was observed to furnish the one-electron oxidized NN-ligand radical concomitantly with conversion of the azide to the corresponding imido (**F**) or amido fragment (**G**) bound to Cr, in the latter case with adventitious H-atom transfer. Using trisyl azide as substrate and 1,2-bis(phenylamido)benzene as ligand, catalytic C–H insertion to provide a benzosultam product **H** was observed, although in modest turnover numbers ($\text{TON} < 5$). The outcome of this particular reaction may be explained by ligand-to-substrate single-electron transfer to generate an imidyl (or nitrene) radical species in the coordination sphere of chromium. Follow-up intramolecular hydrogen atom abstraction and subsequent rebound (or alternatively direct C–H insertion) leads to product formation.

Combining the well-known aminophenol-based redox-chemistry with ever-expanding chemistry related to pincer platforms, and building on expertise in the use of reactive pincer ligand systems,^[38] van der Vlugt et al. developed the $\text{NN}^{\text{H}}\text{O}^{\text{H}}$ ligand **L1**^{H2} (**L1**^{H2} = 2,4-di-*tert*-butyl-6-((2-(pyridin-2-yl)propan-2-yl)amino)phenol). Exchanging the peripheral pyridine for a phosphine donor group provides the corresponding $\text{PN}^{\text{H}}\text{O}^{\text{H}}$ framework **L2**^{H2}. Both ligands readily coordinate to Pd^{II} as the ligand radical L^{SQ} , giving access to crystalline paramagnetic square planar $\text{PdCl}(\text{L}^{\text{SQ}})$ complexes with discrete well-behaved ligand-based electrochemical responses according to



Scheme 3. Ligand-to-substrate single-electron transfer using *o*-phenylenediamine-derived chromium(III) complexes upon reaction with aryl and sulfonylazides, and catalytic formation of benzosultam product H.

cyclic voltammetry, with the potentials for the respective redox-couples subtly dependent on the peripheral donor groups whilst coordinated to Pd^{II}. They have also reported homodinuclear palladium complexes derived from these platforms and close analogs thereof and have studied the magnetochemistry and spectroelectrochemistry of their ligand-radical binding pockets.^[39] Moreover, a route was devised to prepare heterodi- and trinuclear complexes with tunable d⁸–d¹⁰ metal interactions.^[40]

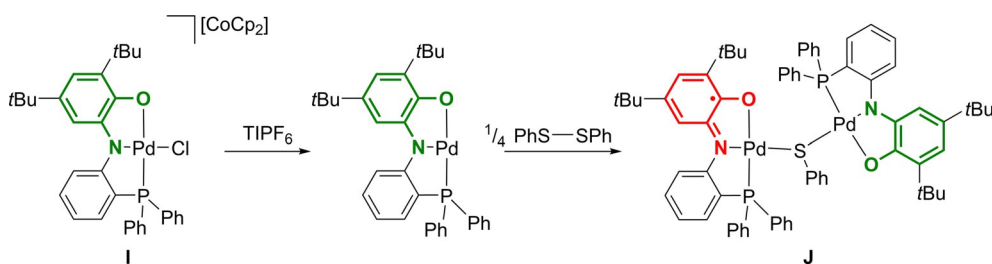
In situ reduction of the PdCl(L^{2ISQ}) complex in the presence of a stoichiometric amount of CoCp₂ as reducing agent generated the fully reduced PNO^{AP} platform I in an overall anionic Pd-complex. Addition of TlPF₆ as chloride removal agent enabled this system to facilitate the homolytic bond cleavage of disulfides through a ligand-to-substrate single-electron-transfer process (Scheme 4).^[41] Using a 1:1 ratio of Pd-complex and diphenyl disulfide, the intermediacy of a free thiyl radical was evidenced by GC-MS analysis, as PhSPh was detected from reaction of the thiyl radical with the benzene solvent after S–S cleavage. Use of di(*tert*-butyl)disulfide allowed for spectroscopic observation of the corresponding disulfide adduct by NMR spectroscopy. The second part of the activated disulfide is transformed into a Pd-bound thiolate, with reformation of the L^{2ISQ} form in the coordination sphere of Pd. Follow-up dimerization with reduced Pd(L^{2AP})-complex resulted in the crystallographically characterized ligand mixed-valent dinuclear species

J (L^{2ISQ})Pd–SPh–Pd(L^{2AP}). Clean formation of the dimeric species was obtained when using a 4:1 ratio of Pd-complex to disulfide substrate.

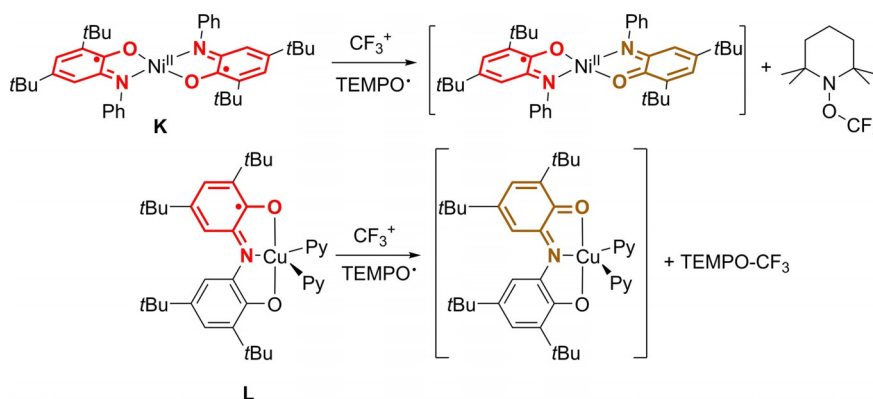
Catalytic Ligand-to-Substrate Single-Electron Transfer

The group of Desage El-Murr, partly in combination with the Fensterbank group, has demonstrated the use of square planar Ni^{II} complex K featuring two aminophenol-based ligands or five coordinate Cu^{II} complex L bearing a redox-active ONO pincer ligand, present in the one-electron oxidized iminosemiquinone (L^{ISQ}) form, as an effective platform for the generation of free trifluoromethyl radicals (CF₃[•]), which formed upon single-electron transfer from a metal-bound iminosemiquinone ligand radical to a source of CF₃⁺ (Scheme 5).^[42] It is postulated that no direct metal–CF₃ bond occurs because the reactivity differs from that of isolated species with this bond present.^[43] Besides radical-radical coupling with TEMPO, catalytic trifluoromethylation of alkynes, heteroaromatics and vinyl silyl ethers was reported as well. The complexes formed after electron transfer were spectroscopically investigated but not isolated.

The concept of selective ligand-to-substrate single-electron transfer can be exploited to generate nitrene radicals in the coordination sphere of, for example, a “redox-inert”^[44] metal ion (Pd^{II}). In situ reduction of the Pd-bound NNO-ligand L^{1ISQ} in



Scheme 4. Ligand-to-substrate single-electron transfer to homolytically cleave disulfides and generate mixed-valent dinuclear Pd-ligand species.



Scheme 5. Selected examples of outer-sphere ligand-to-substrate single-electron transfer to CF_3^+ .

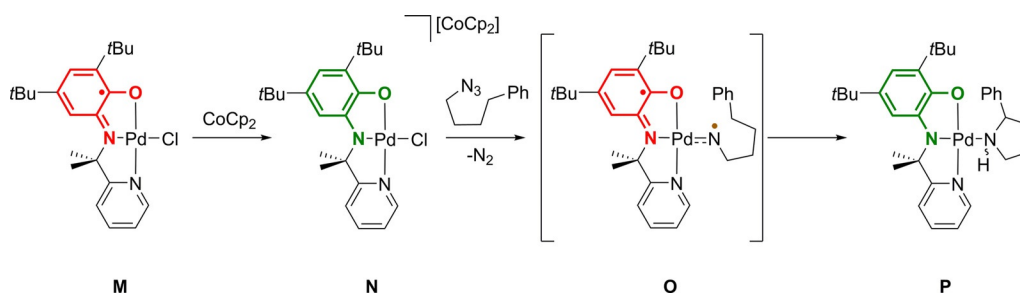
complex **M** to the NNO^{AP} form (**N**) using an equimolar amount of CoCp_2 , followed by activation of the organic azide substrate and irreversible expulsion of dinitrogen, initially generates the corresponding nitrene (Scheme 6). However, single-electron transfer from the ligand to this hypovalent substrate featuring an empty p -orbital can occur to form an open shell singlet “diradical” (nitrene radical-ligand radical) **O**, as confirmed by DFT calculations. This effectively generates a nitrogen-based substrate radical bound to Pd^{II} that is amenable to C–H insertion reactivity, as demonstrated by the formation of the *N*-Boc-pyrrolidine adduct **P** from the benchmark substrate 4-phenylbutyl-1-azide by a two-step H-atom transfer and rebound, as supported experimentally by KIE data and DFT computations, and finally removal of the organic product by di-*tert*-butyldicarbonate (Boc-anhydride).^[45] Although the turnover of this systems under optimized conditions is still modest ($\text{TON} \approx 3$), this proof-of-concept demonstrates the potential for ligand-to-substrate single-electron transfer for radical-type catalysis, even at redox-inert metal centers.^[46]

More recently, van der Vlugt et al. disclosed a well-defined, crystallographically characterized, paramagnetic high-spin ($S = 2$) $\text{Fe}^{\text{III}}(\text{Cl})_2(\text{L}1^{\text{SQ}})$ complex **Q** for the intramolecular $\text{C}(\text{sp}^3)\text{--H}$ amination of a broad range of organoazides, with TONs of up to 620 at 0.1 mol% catalyst loading (Scheme 7).^[47] This system is at least one order of magnitude more active than all other reported systems to date, all of which operate through metal-radical catalysis.^[48–51] The Fe^{III} -complex could be quantitatively recycled and re-used after catalysis. It was established that in situ reduction under the same conditions as for the Pd-

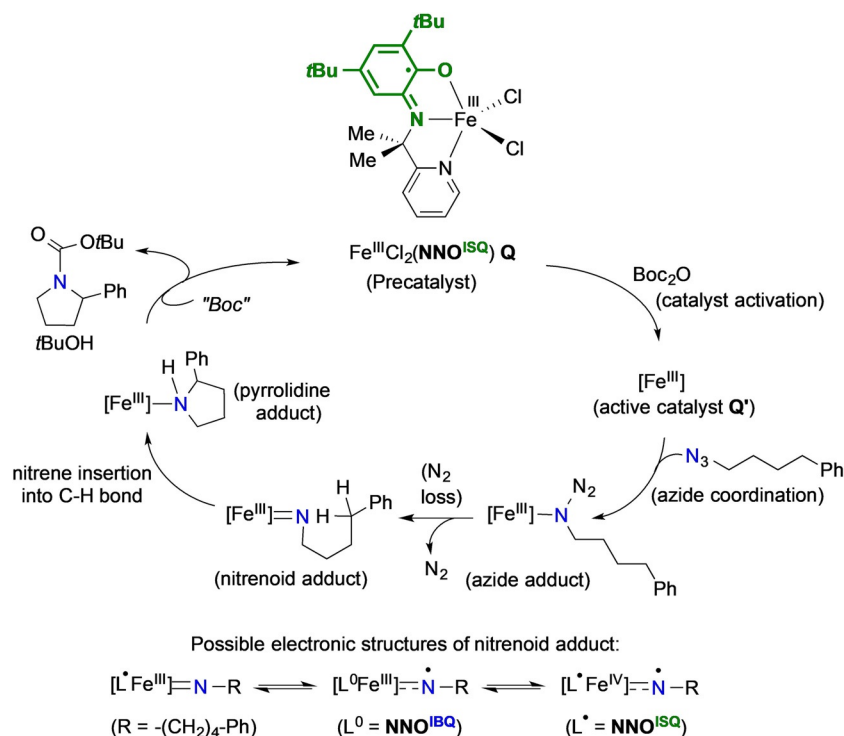
system led to Fe-centered rather than ligand-centered reduction, with subsequent disproportionation to afford a crystallographically characterized homoleptic $\text{Fe}^{\text{II}}(\text{L}1^{\text{SQ}})_2$ complex that was completely inactive for the C–H amination reaction. Furthermore, kinetics the Fe^{III} -based catalysis proved highly unusual, with zeroth order in the organoazide but first order in Boc-anhydride. This hints to a pre-activation step to generate a four-coordinate derivative of the Fe^{III} -system **Q'**, potentially involving reversible reaction of the ligand radical with the Boc-anhydride. The complexity of this system has precluded detailed computational or spectroscopic analyses to date.

Following the same ligand-to-substrate single-electron transfer strategy, Sugimoto, Itoh and co-workers recently described C–H amination catalysis (maximum TON of 10) using the activated substrate tosyl azide and weak C–H bonds as in xanthene.^[52] The catalyst used consisted of a diamagnetic Rh^{III} complex bearing a redox-active ONNO-type ligand, which switches from fully reduced trianionic to dianionic ligand radical **R** upon generation of the nitrene substrate radical bound to Rh^{III} . Follow-up work on this system established that the ligand may be considered chemically non-innocent due to a fragmentation reaction occurring with the tosyl azide in the absence of xanthene substrate, forming **R'**, which is also active for the same C–H amination catalytic reaction (Scheme 8).^[53]

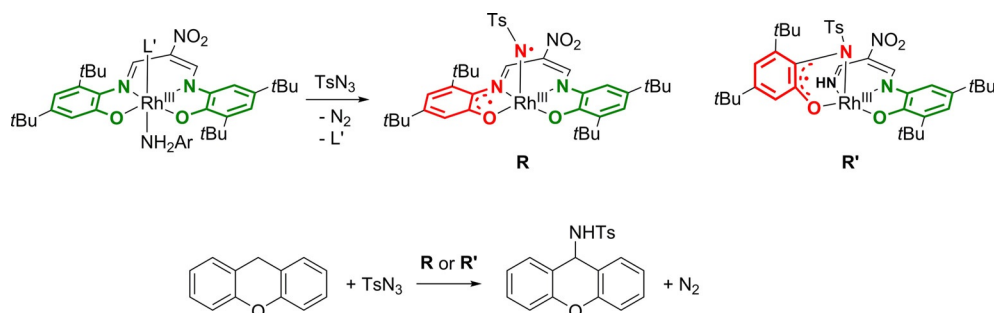
The Desage El-Murr group described the catalytic aziridination of cyclic and acyclic alkenes, non-conjugated dienes and styrenes using tosyliminoiodinane as nitrene source and $\text{Cu}^{\text{II}}(\text{L}1^{\text{SQ}})_2$ as catalyst. This copper-complex **S** has a doublet ground-state due to antiferromagnetic coupling of one of the



Scheme 6. Generation of a nitrene radical in the coordination sphere of Pd^{II} by ligand-to-substrate single-electron transfer and follow-up C–H amination reactivity. Bottom: Fe^{III} -catalyzed C–H amination.

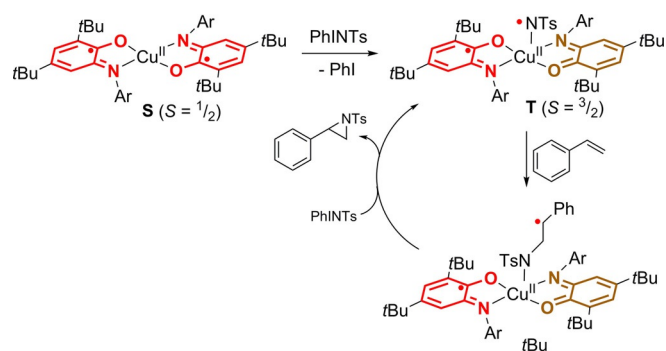


Scheme 7. Postulated cycle for the C–H amination of a broad range of organoazides (4-phenylbutyl azide chosen as an example) using crystallographically characterized Fe^{III}-precatalyst Q.



Scheme 8. A Rh^{III}(ONNO) catalyst for intermolecular C–H amination of xanthene using tosyl azide.

ligand-centered radicals with the unpaired electron at Cu (but an $S = 3/2$ quartet is thermally accessible). A combined spectroscopic and computational study supported a mechanism involving initial formation of a nitrogen-centered nitrene radical **T** after reaction with PhINTs and ligand-to-substrate single-electron transfer. This five-coordinate species has a quartet ($S = 3/2$) ground state. Reaction with a vinylic substrate (styrene in Scheme 9) generates **U** featuring a Cu-bound amido-fragment connected to a carbon-centered radical. HYSCORE experiments at 5 K suggest a doublet ground state for this species because of a spin-flip taking place at the iminosemiquinone ligand. Radical ring-closure results in the organic aziridine product, most likely concomitant with activation of a new PhINTs substrate. Hence, two-state reactivity involving spin-state flipping at the ligand (rather than the metal, which is more commonly observed) is crucial for this catalytic reaction.^[54]

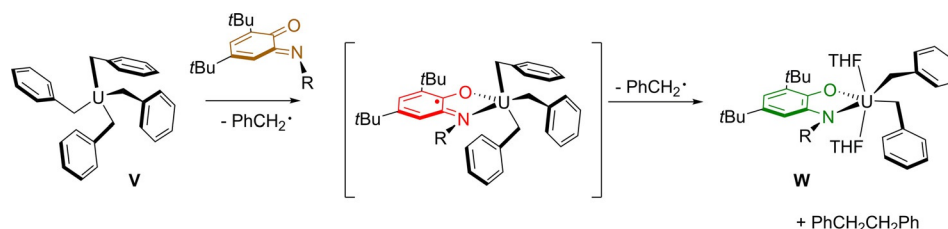


Scheme 9. Copper(II) mediated aziridination of vinylic substrates by ligand-centered two-state reactivity.

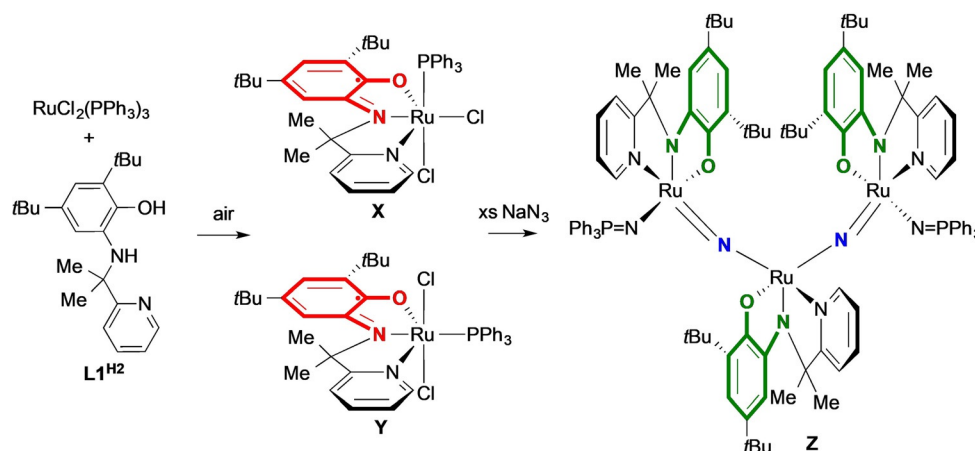
Turning the Tables: Stoichiometric Single-Electron Transfer to a Redox-Active Ligand

There are at least two examples in which the (initial) electron transfer occurs from a substrate to a redox-active ligand rather than, as in the above examples, ligand-to-substrate SET. Notably, such "oxidative" substrate activation is not reported to date for metalloradical-based catalysis. The group of Bart has reported on the radical reductive elimination of 1,2-diphenylethane by the release of a benzyl radical from U^{IV} -tetra(benzyl) complex **V** upon reaction with 3,5-bis(*tert*-butyl)iminobenzoquinone, followed by a second single-electron-transfer event and radical expulsion to yield amidophenolate-bis(benzyl) U^{IV} derivative **W** (Scheme 10).^[55]

The group of van der Vlugt reported the reaction of NaN_3 with both *cis*- and *trans*- $Ru^{III}(Cl)_2(PPh_3)(NNO^{5Q})$ **X** and **Y**, with NNO^{5Q} being the ligand-radical version of a redox-active pincer ligand $NN^H O^H$ ligand **L1**^{H2}.^[56] The final product after reaction in ambient light is a trinuclear complex **Z** featuring bridging nitrido ligands that originate from the sodium azide as well as three fully reduced NNO^{AP} fragments (Scheme 11). Isotope labeled ¹⁵N-azide studies coupled to GC analysis of the formed N_2 by-product strongly suggests multiple events of substrate-to-ligand single-electron transfer. There appears to be much potential to extrapolate this concept of activating substrates by a substrate-to-ligand single-electron transfer to catalytic applications.



Scheme 10. Stepwise single-electron transfer from a U^{IV} (tetra(benzyl)) complex to an incoming iminobenzoquinone ligand to afford complex **W**.



Scheme 11. Formation of a trinuclear ruthenium complex with two bridging nitrides by single-electron transfer from a nitride ligand to the redox-active ligand.

Conclusions and Outlook

Single-electron transfer to or from a redox-active ligand to induce radical-type reactivity on a metal-bound substrate has rapidly emerged in the last ± 5 years. Notable stoichiometric as well as catalytic applications in the area of C–H insertion and alkene functionalization exploit this new concept. Much more exciting reactivity based on selective single-electron transfer between redox-active ligands and metal-bound substrates can be foreseen, with both early and late transition metals, lanthanides as well as possibly also main-group elements. This may offer new ways to accomplish (catalytic) atom- and group-transfer reactions as well as hydroadditions, to name a few important classes of transformations. In this context, it should be noted that also another type of "ligand reactivity", that is, involving proton-responsive ligands, has become prominent in the realm of both noble and base metal–ligand bifunctional substrate activation and catalysis in the last decade.^[57] However, strategies to effectively bridge redox non-innocence and such chemical non-innocence have been only scarcely identified to date.^[58–62] However, if this selective ligand-centered hydrogen-based chemistry could be exploited alongside the established electron-based reactivity of such ligands, this might allow for interesting crossover studies between previously disparate ligand-based reactivity patterns. Ultimately, this offers the foresight of selective and efficient proton-coupled electron transfer^[63] in catalysis. It is therefore deemed only a matter of

time before exciting extensions and novel additions to this field of redox-active ligand-based reactivity are developed.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: non-innocent ligands · radical · redox-active ligands · single-electron transfer · substrate

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