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Manifestations of Noninnocent Ligand Behavior

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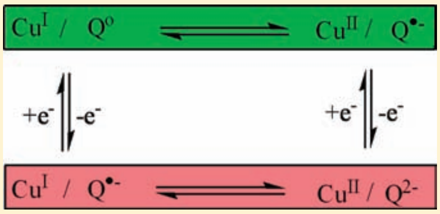
ABSTRACT: The potential of redox-active ligands to behave "noninnocently" in transition-metal coordination compounds is reflected with respect to various aspects and situations. These include the question of establishing "correct" oxidation states, the identification and characterization of differently charged radical ligands, the listing of structural and other consequences of ligand redox reactions, and the distinction between barrierless delocalized "resonance" cases $M^n/L^n \leftrightarrow M^{n+1}L^{n-1}$ versus separated valence tautomer equilibrium situations $M^n/L^n \rightleftharpoons M^{n+1}L^{n-1}$. Further ambivalence arises for dinuclear systems with radical bridge $M^n(\mu\text{-}L^{\bullet})M^n$ versus mixed-valent alternatives $M^{n+1}(\mu\text{-}L^{-})M^n$, for noninnocent ligand-bridged coordination compounds of higher nuclearity such as $(\mu_3\text{-}L)M_3$, $(\mu_4\text{-}L)M_4$, $(\mu\text{-}L)_4M_4$, or coordination polymers. Conversely, the presence of more than one noninnocently behaving ligand at a single transition-metal site in situations such as $L^n{-}M{-}L^{n-1}$ or $L^{\bullet}{-}M{-}L^{\bullet}$ may give rise to corresponding ligand-to-ligand interaction phenomena (charge transfer, electron hopping, and spin–spin coupling) and to redox-induced electron transfer with counterintuitive oxidation-state changes. The relationships of noninnocent ligand behavior with excited-state descriptions and perspectives regarding material properties and single-electron or multielectron reactivity are also illustrated briefly.



1. INTRODUCTION

Referring to redox-active ligands as "noninnocent" has lately become more frequent, especially in the description of chemical reactivity.[1] Originally, this expression was coined by Jørgensen[2] in order to describe the oxidation-state ambiguity of redox-active molecules in their coordination compounds with redox-active transition metals: "Ligands are innocent when they allow oxidation states of the central atoms to be defined".[2] The expression "noninnocent", in contrast, conveys an uncertainty and, literally, an *ambi-valence* of oxidation-state assignments, rendering certain ligands as "suspect". The classical case mentioned by Jørgensen was NO: "The simplest case of a suspect ligand is NO".[2] For example, a combination of electron paramagnetic resonance (EPR) and Mössbauer spectroscopy showed that the "brown ring" ion $[Fe(NO)(H_2O)_5]^{2+}$ from the analytical detection of nitrite or nitrate and alternatively formulated as Fe^I/NO^+,[3] $Fe^{II}/NO^{\bullet}$, or Fe^{III}/NO^- is best described using the latter formulation.[4]

Although noninnocent behavior was recognized early and in several instances, including biochemically relevant systems[5] such as $O_2^{0/\bullet-/2-}$, quinones/semiquinones/catecholates, tetrapyrrole macrocycles (porphyrins, chlorins, and corroles), α-diimines, or α-dithiolenes, the reception of the "NI" word was initially slow.[6] An important aspect concerned the fact that redox-active ligands can behave both in an innocent and in a noninnocent way. This dichotomy will be illustrated in section 8 for diruthenium complexes bridged by azo-group-containing ligands,[7] but even the extremely strong acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has been observed to act as a normal neutral ligand or as partially or fully reduced species (see section 9).[8,9] Ward and McCleverty have thus emphasized the necessity of considering the particular coordination situation and referring to "noninnocent behavior" rather than, per se, "noninnocent ligands" (NILs).[10]

This article uses the "noninnocent" descriptor exclusively in the sense of *redox* noninnocence. Recently, the term "noninnocent" has also been applied to other, non-redox-active ligands in order to indicate the perturbation of metal coordination by the unexpected reactivity of ligands in response to external stimuli.[11]

While the oxidation-state concept can come under criticism from time to time,[12] there is a clear recognition of its usefulness beyond mere electron bookkeeping. The "art of establishing physical oxidation states"[13] by determining the electron configuration through combined experimental and computational efforts cannot be discarded by invoking the assumed meaninglessness of oxidation states for largely covalently bonded cases (cf. section 5).

2. SURVEY OF NILs

In addition to classical NO[2,4] (**I**) and O_2 (**II**, E = O), several kinds of ligands have been recognized as redox-ambivalent: α-diimines such as 1,4-diazabutadienes (**III**, E = NR),[14] dialkylglyoximes, 2-pyridylcarbaldimines, pyridine-2,6-diimines, *o*-quinonediimines (**IV**, E = NR), 2,2′:6′,2″-terpyridines and 2,2′-bipyridines,[15−17] α-diketo compounds, especially *o*-quinones (**IV**, E = O),[18,19] and α-dithiolenes (**III**, E = S).[20] Other, early established candidates include azo compounds (**II**, E = NR)[21] and polycyano ligands such as tetracyanoethylene (TCNE; **V**, CN substituents) or TCNQ (see Chapter 9).[8,9,22] 1,2,4,5-Tetrazines (**VI**)[23] or α-azocarbonyl ligands[24] can also serve as NILs. From biochemical research came evidence that O_2,[25] flavins,[26] tetrapyrrole macrocycles,[28] phenolates,[29,30] and pterins[26b] qualify as redox NILs.[5] Redox-active ligands from organometallic chemistry, i.e., involving metal−carbon bonding, have also been

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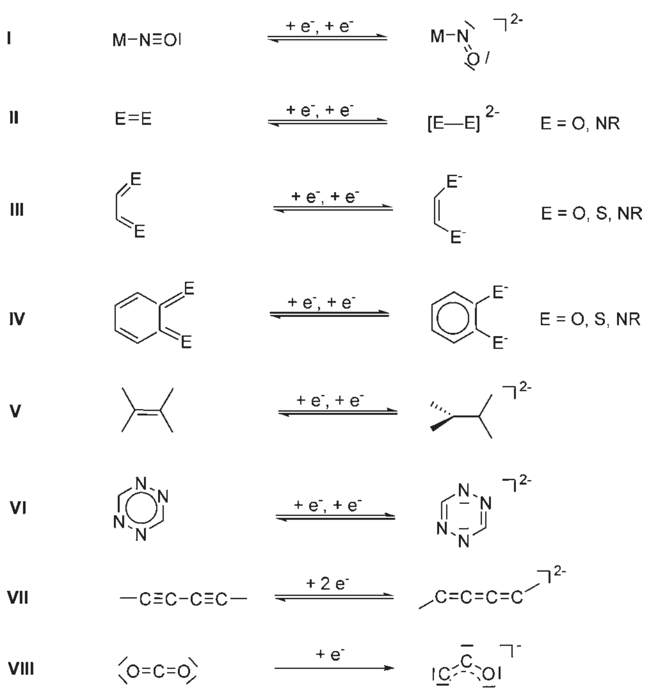
Scheme 1. Representative Structural Changes Associated with Electron Transfer to Selected Molecules, Including Potentially Redox-Active Ligands

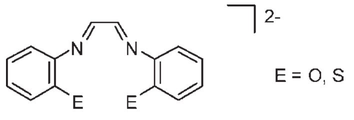


developed, including especially unsaturated C_n chains (e.g., **VII**).[27] The characteristic structural changes occurring for redox-active molecules, including NILs, are illustrated for selected cases in Scheme 1.

Research on noninnocently behaving ligands in coordination compounds can be performed in different directions:

(i) One approach is to identify and establish the noninnocent behavior, especially in a biochemical setting[5] or, for insufficiently documented cases, from the earlier literature.[31] One well-studied case has been confirmation of the phenolato ligand instead of copper metal oxidation during the enzymatic action of galactose oxidase.[5,29,30]

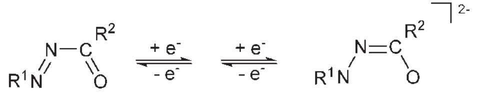
(ii) Another approach consists in the recognition or design and development of new ligands[24,32] and their metal complexes, followed by the characterization of native and reduced/oxidized states (often via spectroelectrochemistry),[33] including the "where is the electron?" question.[25e,34,66] Examples include the recognition and study of the redox activity of deprotonated tetradentate glyoxalbis(2-hydroxylanil)[32b] or glyoxalbis(2-mercaptoanil) ligands (**IX**)[32d]



IX

and the conjugative combination of electron-affine carbonyl and azo functions in α-azocarbonyl ligands (**X**).[24]

X

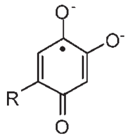


(iii) A further approach is the use of thus characterized systems for organic/organometallic transformations (including catalysis)[35−39] and for the construction of materials with attractive physical properties such as magnetic exchange phenomena, electrical conductivity, optical properties, or bistability.[40,41,71]

3. RADICAL FORMS OF REDOX-ACTIVE LIGANDS

Single-electron transfer involving noninnocently behaving redox-active ligands will lead to radical ligands, as either intermediates or final products. Most, but not all, such species (see the singlet diradicals discussed in section 11) produce paramagnetic materials, and as Collman said in an article[42] cited by the Editor of *Organometallics*, "... chemists [have] avoided working with paramagnetic compounds, because in most cases, paramagnetism obviates a very useful analytical tool: NMR. ... I foresee ... the exploitation of the unusual catalytic and other reactivity that can be found in certain paramagnetic states."

As reviewed in 1987,[43] *radical monoanions*, routinely obtained by the one-electron reduction of neutral precursors or by the one-electron oxidation of dianions, are among the most common radical ligands for main-group and transition-metal centers, either as small ions such as $O_2^{\bullet-}$ (superoxide) or as larger π systems such as pyridine-type heterocycles. The presence of additional negative functions such as RO^- or R_2N^- can give rise to *radical-dianion* ligands such as **1** or **2**[44] or to *radical trianions* such as those in reduced metalloporphyrins;[45] however, even small such species like $N_2^{\bullet 3-}$ are known to act as ligands in coordination compounds.[46,47] From such recognition followed the development and identification of related new species like $NO^{\bullet 2-}$.[47,48] *Neutral radical* ligands are generally less basic but do exist in the form of $NO^{\bullet}$,[49] $R_2NO^{\bullet}$,[50] verdazyls,[51] or 1-methylpyrazinyl (mpz$^{\bullet}$, **3**);[52] even *radical cations* can serve as ligands, as has been shown for the 2,2′-bipyridine/1,1′-dialkyl-4,4′-bipyridinium hybrid **4**.[53]



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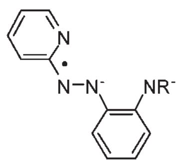

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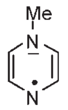

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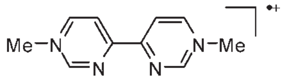

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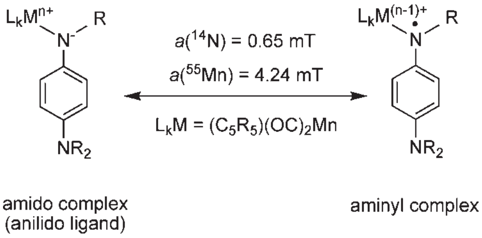
4. "FALSE" METAL OXIDATION STATES

An occasional consequence from the presence of unrecognized noninnocently behaving ligands is the erroneous assignment of "unusual" oxidation states to metals in coordination compounds. As an example, the Ga^{II} state had been invoked[54a] for a mononuclear complex [Ga^{II}(*t*Bu-dab^{2-})(*t*Bu-dab)] when actually a [Ga^{III}(*t*Bu-dab$^{\bullet-}$)(*t*Bu-dab^{2-})] situation was present (*t*Bu-dab = 1,4-di-*tert*-butyl-1,4-diazabutadiene).[54b] One-electron-reduced sensitizer complexes such as [Re(CO)$_3$Cl(bpy)]$^-$ or

$[Cu(dpp)_2]$ (dpp = 2,9-diphenyl-1,10-phenanthroline) were similarly addressed as Re^0 or Cu^0 species,[55,56] respectively, when actually the α-diimine chelate ligand was the site of electron acceptance and the metals occurred in their more conventional Re^I (d^6) and Cu^I (d^{10}) configurations.[57,58]

A more challenging question was the identification of organometallic compounds $Mn(CO)_2(C_5R'_5)(ER_n)$, where ER_n = SR or NHR. Originally formulated as ($^{\bullet}ER_n$) radical-containing organomanganese(I) species (with d^6 configuration implied),[59] the EPR study showed a predominant Mn^{II} (low-spin d^5) character with more conventional $^{-}ER_n$ ligands.[60,61] Approaching the radical stabilization by using deprotonated *p*-phenylenediamine as the $^{-}ER_n/^{\bullet}ER_n$ redox-active ligand, it was possible, however, to achieve a rather balanced resonance situation (1) between both the $Mn^I/^{\bullet}ER_n$ and $Mn^{II}/^{-}ER_n$ formulations.[61] The ^{55}Mn hyperfine coupling was found at 4.24 mT, i.e., about two thirds the value for other low-spin Mn^{II} species,[62] whereas the ^{14}N coupling was correspondingly lowered to 0.65 mT[61] from about 1.2 mT in genuine aminyl radicals.[63]



(1)

While the question of aminyl radical versus amido species as noninnocently behaving ligands was also discussed later in a number of instances,[61,64,65] it has been overshadowed by the formally analogous but biochemically more relevant case (2) of coordination compounds with the phenolato/phenoxyl ligand redox system, for which excellent reviews are available.[29,30]

(2)

5. ELECTRON DELOCALIZATION OR VALENCE TAUTOMERISM INVOLVING NILs

The example in the resonance formulation (1) shows the EPR evidence for approximately equibalanced resonance forms, in contrast to barrier-separated radical and metal-spin-centered species as in system (3) vide infra.

It is important to realize that the valence isomeric alternatives can involve either two (or more) different species in equilibrium, e.g.,

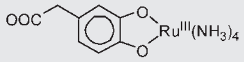
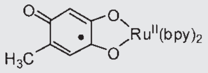
$$M^n/L^n \rightleftharpoons M^{n+1}/L^{n-1}$$

separated by an activation barrier, or two (or more) resonance forms

$$M^n/L^n \leftrightarrow M^{n+1}/L^{n-1}$$

describing only *one* species with *one* energy potential minimum. In the latter case, the main contribution(s) may be established experimentally and/or computationally.[13]

Table 1. *g* Factors of Two Ruthenium Compounds

	 (low-spin d^5/catecholate)	 (low-spin d^6/semiquinone radical)
g_1	2.722	2.0053
g_2	2.722	2.0053
g_3	1.889	1.997
Δg^a	0.833	0.0083
$\langle g\rangle^b$	2.476	2.0025
ref	68e	44a

[a] $\Delta g = g_1 - g_3$. [b] $\langle g\rangle = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$.

As in the organomanganese example (1) but in contrast to the valence tautomeric Cu−Q system (3) shown below, the situation of ruthenium quinone complexes corresponds to the barrierless "resonance structures" model.

$$Ru^{II}/Q^{\bullet-} \leftrightarrow Ru^{III}/Q^{2-}$$

The modification of quinones and ancillary ligands L in $[Ru(Q)(L_n)]$ causes either more metal-centered or more ligand-centered spin, and calculations have demonstrated that "often, the true situation in a given complex may be intermediate between integer oxidation numbers, and the structural data are expected to reflect this".[66b] Extensive studies have shown that intramolecular electron shifts in mononuclear and dinuclear ruthenium complexes with quinonoid ligands can exhibit particularly intriguing patterns.[39,66−68]

Several physical methods are available to establish the most appropriate oxidation (and spin) state descriptions in a transition-metal coordination compound with redox-active ligands. These can include X-ray crystallography,[18,19] vibrational spectroscopy (IR/Raman), EPR[43] and NMR, UV−vis−near-IR (NIR), and X-ray absorption spectroscopy (XAS).[15b] Electrochemical information on redox potentials and mechanisms is particularly useful when supported by spectroscopic characterization (=spectroelectrochemistry[33]), reflecting the energy and reactivity associated with the electronic structures. Computational reproduction of experimental data will typically confirm the assignments and provide further insight.

The EPR information is helpful in the following sense: Based on established expressions[43a] for the *g* value that feature the spin−orbit coupling constants ξ of the participating atoms as factors, the *g* values and especially the *g* anisotropy $\Delta g = g_1 - g_3$ have been used as approximate measures of participation of the heavy transition metal with its high ξ value at the singly occupied molecular orbital (SOMO).

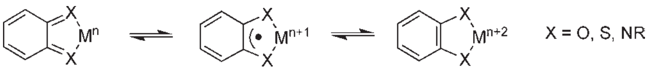
Two extreme cases (Table 1) illustrate that range.

Although both entries in Table 1 are $S = {}^1/_2$ species, the *g* factor anisotropy Δg as well as the average $\langle g\rangle$ reflect the dominant [ruthenium(III) catecholate] versus vanishing [ruthenium(II) semiquinone] participation of the heavy metal at the SOMO.

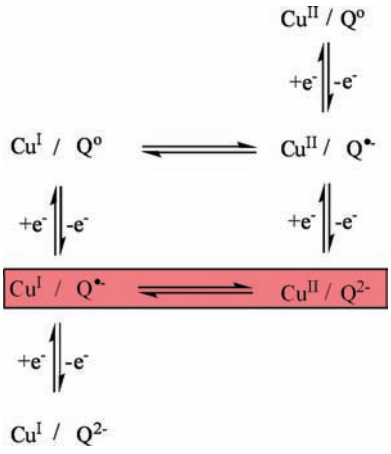
A wide range of data has thus been collected[66a,69] for paramagnetic ruthenium compounds with Ru^{III}, $Ru^{II}(NIL^{\bullet})$, and Ru^I centers, which allows for an assessment of new species with intermediate Δg and $\langle g\rangle$ values.

The occurrence of a barrier between two (or more) "redox isomeric" = "valence tautomeric" forms involving typically

Scheme 2. Valence Tautomer Equilibria of Complexes with *o*-Quinonoid Chelate Ligands



Scheme 3. Cu^n/Q^m System (Q = *o*-Quinone, $Q^{\bullet-}$ = Semiquinone, and Q^{2-} = Catecholate)

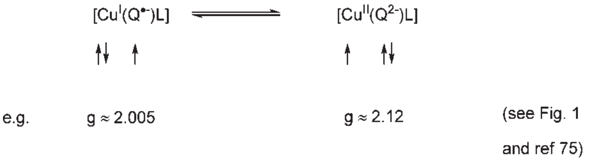


one-electron shifts between a metal and a (noninnocent) ligand has been reviewed a number of times[70] and has been discussed in light of possible applications (bistability), especially when accompanied by spin-crossover effects.[40,71] Valence tautomers have been observed for several such species, including iron, manganese, cobalt, and copper complexes of *o*-quinonoid (1,2-dioxolene) ligands (Scheme 2).[70,75]

While the cobalt systems offer the additional complication (and advantage) of potential spin crossover,[71] the copper systems were discussed with reference to spin-coupling phenomena[13] and to enzymatic mechanisms in amine oxidases. Scheme 3 shows alternatives for the copper/quinone combination (Scheme 3).[72]

The $Cu^{II}/Q^{\bullet-}$ and Cu^I/Q^0 forms have been identified for selected cases[78,79] via structure determination, magnetism, electrochemistry, and spectroscopy, and the copper(II) semiquinone compounds are distinguished by ferromagnetic coupling.[78] The Cu^{II}/Q^{2-} and $Cu^I/Q^{\bullet-}$ forms were observed in temperature-dependent equilibrium (3), first within amine oxidase enzymes[74] and then for low-molecular-weight complexes.[75,76]

The large structural and chemical difference[73] between Cu^I and Cu^{II} gives rise to a significant barrier between corresponding valence tautomeric forms, and the occurrence of temperature-dependent equilibria (3) between copper(I) semiquinone radical species and copper(II) catecholate complexes has been observed a number of times.[75,76] The clear distinction between both such configurations has also been observed during the quenched enzymatic cycle of amine oxidases,[74] suggesting the formation of O_2-activating copper(I) via such a process.[77]



(3)

Density functional theory (DFT) calculations (Figure 1) confirm the existence of valence tautomers for suitable models.[80]

6. CONSEQUENCES OF ELECTRON TRANSFER TO AND FROM REDOX-ACTIVE LIGANDS

The question as to which oxidation-state alternative is "correct" does not simply constitute l'art pour l'art because the oxidation state of a ligand will determine various experimental properties.

(i) Structural variations of NILs and other prototypical molecules have been established; some of them are depicted in Scheme 1. The popular use of metrical parameters to establish ligand charge states and thus, by implication, metal valence[14e,15−25] may have limitations, however, when extensive delocalized bonding occurs or when steric effects compete with the electronically favored structure.[81]

(ii) Spectroscopic features will reflect the oxidation state of the ligands, often by implication from, e.g., EPR, XAS, or Mössbauer studies of the metal electronic configuration.[4,15]

(iii) Electron transfer to or from the ligands will strongly alter their acid/base properties, which will lead not only to a changed proton affinity but also to additional coordination activities. As a result, the nuclearity of complexes may be affected by electron transfer with increasing negative charge, favoring the formation of oligonuclear systems (Scheme 4).[9b,43a,82]

(iv) The binding mode of an ambidentate ligand toward a metal center may be affected by its charge state, changing, e.g., between different donor sites[83a] or between π- and σ-donor coordination (ligand-based molecular hysteresis).[83b]

(v) Elementary as well as multistep reactions may be influenced by the oxidation states of the ligand. Depending on the extent of ligand/metal interaction (electron delocalization and partial covalency), the metal and its coligands can display altered reactivity as an indirect result of the ligand's redox activity. We have thus coined the term "18 + δ valence electron configuration"[84,85] for those examples in which a predominant but not exclusive electron addition to the NIL of an 18 valence electron complex causes significant activation at the metal site, e.g., in terms of substitution[86] or addition (Scheme 4).[87] δ can be assessed experimentally through EPR or IR vibrational information and may be correlated with the reactivity[84] (which can proceed catalytically if the conditions for electron-transfer catalysis are met[82c]).

7. SEPARATED METAL BINDING AND ELECTRON-TRANSFER ACTIVITY OF NILs

While it is most commonly a spin-bearing donor atom (like O or N) that binds the transition metal in a complex with NIL(s), there are cases where the metal binding and electron-transfer site are spatially and electronically separated. Typical examples are π-radical ions with metal-binding phosphanyl substituents, which show little conjugation to the spin-bearing π system (**5**).[88,89] Other examplex are π systems involving a reducible tetrazine ring connected to spin-free but metal−metal-bridging pyridyl functions **6**,[90] or reducible quinoxaline components (boxed-in) versus various chelating functions in formal conjugation (**5**, **7**, and **8**).[89,91,92] The well-known dipyrido[3,2-*a*:2′,3′-*c*]phenazine (**7**, dppz) is such an example;[91] its metal complexes have been

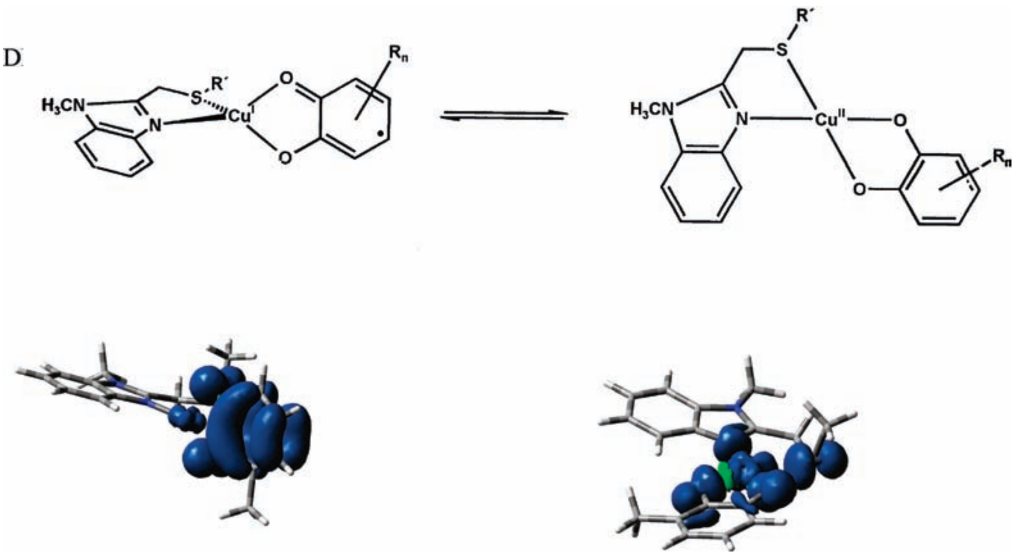
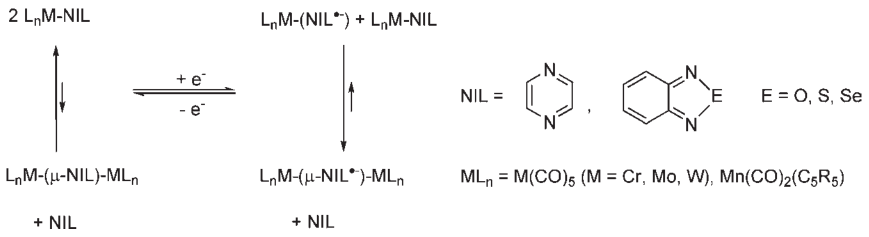
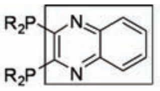


Figure 1. Valence tautomer equilibrium[75] $LCu^{I}(Q^{\bullet-}) \rightleftharpoons LCu^{II}(Q^{2-})$ (R', R_n = CH_3) with DFT-calculated optimized structures and spin densities.[80]

Scheme 4. Shifted Mononuclear/Dinuclear Coordination Equilibria as a Result of Noninnocent Bridging Ligand Behavior[82]



used for the purpose of medium-dependent luminescence ("molecular light switch").[93]



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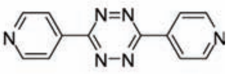

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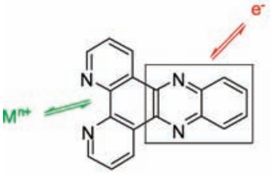

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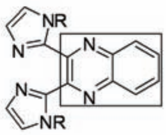

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8. DINUCLEAR SITUATIONS WITH REDOX-ACTIVE BRIDGING LIGANDS

The potential of NILs to act as bridging ligands for oligonuclear coordination compounds (sections 8−10) and their possible occurrence more than once in a metal complex (sections 11 and 12) can create additional opportunities for valence ambivalence.

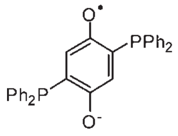
Starting with NIL-bridged dinuclear arrangements involving two equivalent redox-active transition-metal centers, one of the most intriguing questions is whether open-shell intermediates are to be formulated as NIL-radical-bridged homovalent species or as nonradical-bridged mixed-valent systems (4).[94,95]

$$\underset{\text{radical bridge}}{[L_nM^x(\mu\text{ -NIL}^{\bullet-})M^xL_n]} \quad \text{or}$$

$$\underset{\text{localized/delocalized mixed valence}}{[L_nM^{x+1}(\mu\text{ -NIL}^{2-})M^xL^n]/[L_nM^{x+0.5}(\mu\text{ -NIL}^{2-})M^{x+0.5}L_n]} \qquad (4)$$

Mixed-valent compounds have played a significant role in the understanding of electron transfer in general,[96] and they continue to be investigated[97] inter alia for possible applications in molecular electronics.[98] Like many radical ions and their metal complexes, mixed-valent compounds are often distinguished by absorptions in the NIR region of the spectrum,[99] and the correct assignment of oxidation states thus has to rely on additional information such as the spin distribution from EPR spectroscopy.

An early study of alternatives (4) involving diastereoisomeric[94] dinuclear bis(2,2′-bipyridine)ruthenium complexes of *p*- and *o*-semiquinone ligands **9** and **10** has shown two-step one-electron transfer in both cases, with the (3+) intermediates absorbing in the NIR region around 1200 nm. However, additional information from EPR spectroscopy was necessary[94] to identify the intermediates as diruthenium(II) semiquinone compounds, ruling out the dianion-bridged diruthenium(II,III) mixed-valent alternative. According to the exposition in Chapter 5 as illustrated in Table 1, the small *g* factor anisotropy $1.98 < g_1, g_2, g_3 < 2.05$ proved the absence of significant participation from the ruthenium ions with their high spin−orbit coupling constants at the SOMO.[94]



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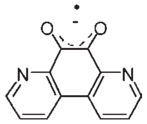

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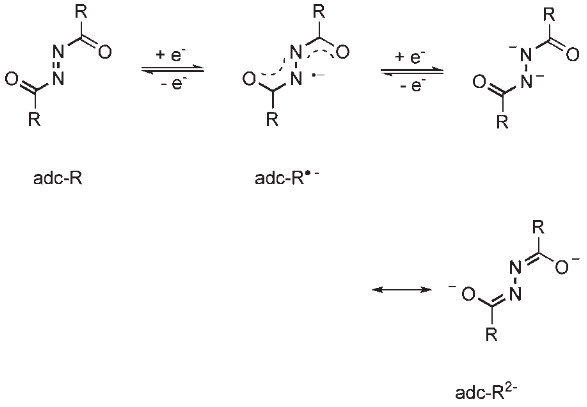
Following the study[94] of $\{(\mathbf{9})[\mathrm{Ru(bpy)_2}]_2\}^{3+}$ and $\{(\mathbf{10})[\mathrm{Ru(bpy)_2}]_2\}^{3+}$, other diruthenium examples containing quinone-type[68,100] and organometallic bridges[27,95] have been described.

Azodicarboxylic esters and related molecules adc-R (eq 5) constitute very special ligands[7,21,101] because they exhibit (i) a quinone-type two-step redox behavior, (ii) a π-conjugated bischelate function, (iii) a small 6π-center system of which four centers are coordinating, (iv) a radical intermediate stable against disproportionation, (v) resonance stabilization of the dianionic form (cf. the aromatic catecholates), (vi) an "S frame" conformation s-cis/E/s-cis, which allows for a rather short M−M distance ($\approx$5 Å) despite molecule bridging,[7c] (vii) a tuning potential through the substituents R at the noncoordinating carbon π centers (e.g., donor or acceptor substitution),[7] and (viii) the possibility of introducing additionally coordinating groups R, leading, e.g., to bis-tridentate NILs.[102]



(5)

An investigation of complexes $[(\mathrm{bpy})_2\mathrm{Ru}(\mu\text{-adc-R})\mathrm{Ru}(\mathrm{bpy})_2]^k$, especially with k = 3+ displaying unusually strong NIR absorption,[7,101] has shown electrochromism and optical attenuation around 1550 nm as required for wavelength-division multiplexing.[103] An additional remarkable feature of these complexes is the pronounced variability of their EPR spectroscopically determined spin distribution between the $\mathrm{Ru^{II}(adc\text{-}R^{\bullet-})Ru^{II}}$ (radical, **A**) and $\mathrm{Ru^{II}(adc\text{-}R^{2-})Ru^{III}}$ (mixed-valency, **B**) alternatives (Scheme 5 and Table 2), depending on the donor or acceptor substituents R. Related systems $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-dih-R})\mathrm{Ru}(\mathrm{acac})_2]^m$, specifically with m = 1, dih-R^{2-} = 1,2-bis(diiminoacyl)hydrazido(2−) involving all-N-donor bridges (Scheme 5), have been reported as products of the reductive ring opening of tetrazines,[104] revealing again intense NIR bands (Figure 2) around 1400 nm but ligand-centered spin due to the lower electronegativity of N versus O.

The corresponding anions $[(\mathrm{acac})_2\mathrm{Ru(adc\text{-}OR)Ru(acac)_2}]^-$ ($\lambda_{\max}$ = 2000 nm) display mixed-valent spin ($\mathrm{Ru^{III}/Ru^{II}}$), as a consequence of the two-electron reduction of the bridge.[101b]

Scheme 5. Radical-Anion-Bridged Homovalent Formulation (A, Left) and Mixed-Valent Alternative (B, Right)[7a]

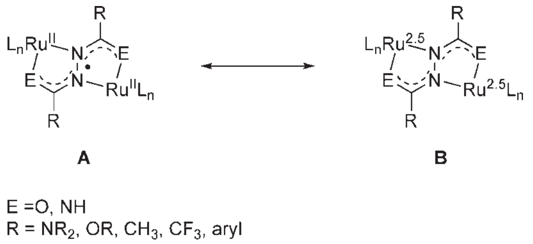


Table 2. Resonance Contributions (Scheme 5) as a Function of Component Variation

E	L_n	R	charge	predominant form	ref
NH	$(\mathrm{acac})_2$	aryl	1−	**A**	104
O	$(\mathrm{acac})_2$	OR	1−	**B**	101b
O	$(\mathrm{bpy})_2$	acceptor ($\mathrm{CF_3}$, COOR)	3+	**B**	7a, 7c
O	$(\mathrm{bpy})_2$	donor ($\mathrm{NR_2}$, OR, R)	3+	**A/B**	7a, 7b

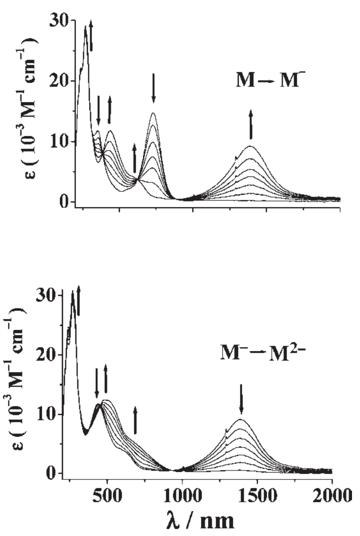
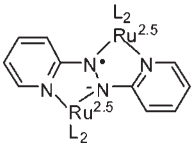


Figure 2. Spectral response during the stepwise ligand-centered reduction of M = $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-dih-Ph})\mathrm{Ru}(\mathrm{acac})_2]$ [dih-Ph = 1,2-bis(diiminobenzoyl)hydrazido, rac isomer; from ref 104]: NIR absorption of the monoanionic intermediate.

In other words, the mixed-valent form **B** requires a completely (two-electron) reduced bridge, which is favored (i) by acceptor substituents R, (ii) by the more electronegative heteroatom E = O instead of E = NH, and (iii) by $\mathrm{Ru^{III}}$-stabilizing acetylacetonato (2,4-pentanedionato) ligands $\mathrm{acac^-}$.

The NIL radical state and the metal−metal mixed-valent situation do not have to be mutually exclusive alternatives, as might perhaps be inferred from above. Using $\mathrm{Ru(acac)_2}$ complex fragments and bridging 2,2′-azobis(pyridine) (abpy), we could characterize two (meso and rac) diastereomeric neutral compounds $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-abpy})\mathrm{Ru}(\mathrm{acac})_2]$, which clearly contain a bond order of 1.5 for the azo function (d = 1.37 Å),[81] suggesting[105] an $\mathrm{abpy^{\bullet-}}$ NIL bridge and thus two mixed-valent $\mathrm{Ru^{2.5}}$ metal centers in $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-abpy})\mathrm{Ru}(\mathrm{acac})_2]$ (eq 6).

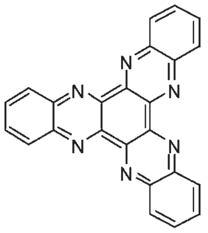
Strong spin−spin interaction leads to a diamagnetic ground state and to a relatively high energy NIR absorption at about 840 nm ($\varepsilon = 28\,000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$).[81] It will be discussed below (section 13) that this description corresponds to the excited-state formulation for charge-transfer excited-state homovalent dinuclear complexes (see eqs 13 and 14). In keeping with the noninnocent character of the abpy bridge, the oxidation and reduction of $[(\mathrm{acac})_2\mathrm{Ru}(\mathrm{abpy})\mathrm{Ru}(\mathrm{acac})_2]$ occur partially at the NIL bridge.[81b] Bonvoisin and co-workers have recently shown that such behavior can also occur with other diruthenium compounds, involving cyanamido functions.[106]



(6)

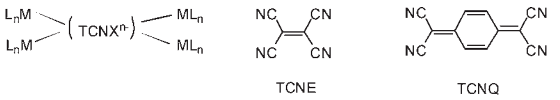
9. NIL BEHAVIOR IN COMPLEXES OF HIGHER NUCLEARITY

Tri- and tetranuclear complexes with redox-active ligands have frequently been studied in connection with mixed-valence chemistry.[107] Thus, ligands such as **11** give rise to $\mathrm{Ru^{III}Ru^{II}Ru^{II}}$ and $\mathrm{Ru^{III}Ru^{III}Ru^{II}}$ mixed-valent intermediates, while their reduction produces radical complex species with the spin mainly on the NIL bridge.[108]



11

Not only can the very strongly π-accepting and often noninnocently behaving TCNX ligands (TCNX = TCNE or TCNQ)[22] form mononuclear σ(N)- or π(CC)-coordinated radical complexes,[83b] but they can bind up to four (eq 7) redox-active (or redox-inactive) transition-metal complex fragments ML_n in either discrete complexes[8,9,22] or coordination polymers.[41]



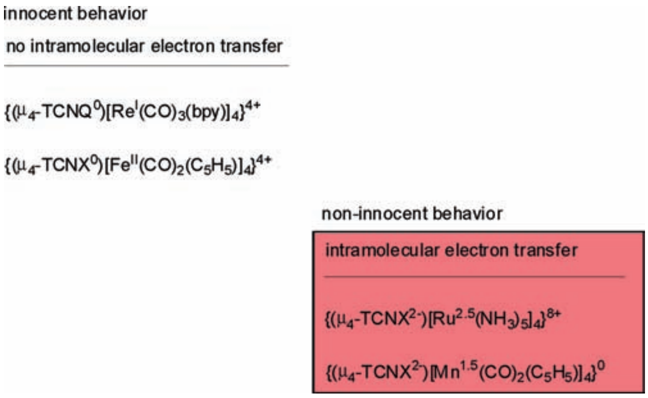
12 **13**

(7)

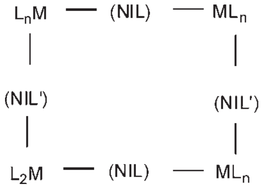
A dichotomy (Scheme 6) involving either innocent behavior (unreduced TCNX and unoxidized ML_n) or noninnocent behavior with significantly reduced TCNX (TCNX^{n-}) and at least partially oxidized ML_n has been documented using structure determination, spectroscopy, electrochemistry, and DFT calculations.[8,9]

For instance, $\{[(\mu_4;(\eta^1)_4\text{-TCNQ})[\mathrm{Re(bpy)(CO)_3}]_4\}^{4+}$ contains rhenium(I) and TCNQ^0,[8a,b] while the species $\{[(\mu_4;(\eta^1)_4\text{-TCNX})[\mathrm{Ru(NH_3)_5}]_4\}^{8+}$, TCNX = TCNE or TCNQ, include $\mathrm{Ru}^{2.5}$ centers bridged by TCNX^{2-}, arranged in a "dimer-of-mixed-valent dimers" framework.[9c,e,f]

Scheme 6. Dichotomy of Innocent[8] or Noninnocent[9] Behavior of TCNX Ligands in Tetranuclear Complexes



Tetranuclear complexes containing noninnocently behaving ligands have also been studied for molecular squares and rectangles (eq 8) with NIL bridges.[109−112] Rhenium(I),[109,110] platinum(II),[111] and platinum(IV)[112] compounds $(\mathrm{L}_n\mathrm{M})_4(\mu\text{-NIL})_2(\mu\text{-NIL}')_2$ with NIL or NIL′ = 4,4′-bipyridine, 2,2′-bipyrimidine, or anthracene-1,8-diyl as reducible or oxidizable bridges have been characterized with respect to the electron-transfer sequence of the bridging moieties.[111]



(8)

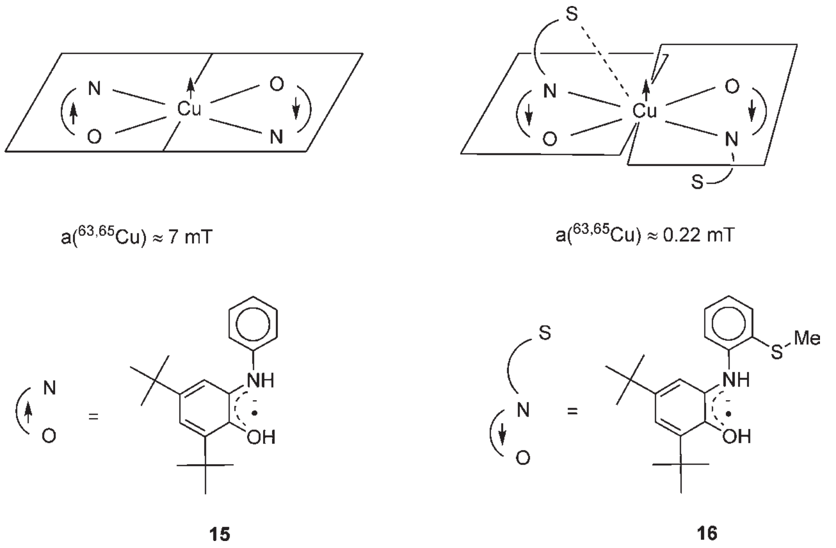
10. REDOX-INDUCED (COUNTER) ELECTRON TRANSFER IN COORDINATION COMPOUNDS

Surprisingly, the reversible one-electron reduction of $\{[(\mu_4;(\eta^1)_4\text{-TCNX})[\mathrm{Ru(NH_3)_5}]_4\}^{8+}$ produced paramagnetic (7+) ions that exhibited ligand-centered spin, according to a $(\mathrm{TCNX}^{\bullet-})(\mathrm{Ru^{II}})_4$ formulation (eq 9).[9c]

$$[(\mu_4;(\eta^1)_4\text{-TCNX}^{2-})(\mathrm{Ru}^{2.5})_4]^{8+}$$
$$\underset{+\mathrm{e}^-}{\overset{-\mathrm{e}^-}{\rightleftharpoons}} [(\mu_4;(\eta^1)_4\text{-TCNX}^{\bullet-})(\mathrm{Ru^{II}})_4]^{7+} \quad \mathrm{Ru} = [\mathrm{Ru(NH_3)_5}] \tag{9}$$

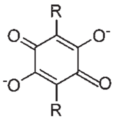
Such "counter-electron-transfer" behavior is not uncommon in NIL chemistry; it can be observed when transition-metal coordination compounds with noninnocently behaving ligands contain more than one redox-active component (ligand or metal). It is possible then to have oxidation-state changes of one component in the opposite direction of the redox reaction of the whole complex (e.g., oxidation of metal or ligand through reduction, i.e., "oxidation leading to reduction");[113] conversely, reduction of metal or ligand can occur through oxidation of the complex. A theoretical treatment of this phenomenon has appeared,[113a] while Miller and Min have recently surveyed examples and referred to this effect as "redox-induced electron transfer".[113b]

Scheme 7. Switched Three-Spin Interaction as a Result of S-Coordination and Twisting[118]



Typically, the combination of two transition metals and one quinone-type NIL bridge **14** can give rise to the effect mentioned above, e.g.[113b]

$$[\mathrm{LCo^{II}}(\mu\text{-}\mathbf{14}^{2-})\mathrm{Co^{II}L}] \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [\mathrm{LCo^{III}}(\mu\text{-}\mathbf{14}^{3-})\mathrm{Co^{III}L^+}] \qquad (10)$$



$\mathbf{14}^{2-}$

Combining vice versa one transition metal and two NILs can give rise to a similar effect, e.g., metal reduction through oxidation of the complex:[44b]

$$[(\mathbf{2})\mathrm{Os^{IV}}(\mathbf{2})] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(\mathbf{2}^+)\mathrm{Os^{III}}(\mathbf{2}^+)]^+ \qquad (11)$$

Typically, the formulation of diamagnetic forms is based on structure/oxidation state correlations (Scheme 1),[19,105] while the paramagnetic species can best be characterized through EPR spectroscopy.[44b,66a] The above-mentioned example (eq 9) also relies on structural (+DFT) and EPR spectroscopic evidence;[9c,e] it illustrates the occurrence of fractional oxidation states and less common stoichiometries.

11. SYSTEMS WITH MORE THAN ONE REDOX-ACTIVE LIGAND

The examples $(\mathrm{L}_n\mathrm{M})_4(\mu\text{-NIL})_2(\mu\text{-NIL}')_2$ (eq 8) include a further aspect of the coordination chemistry of NILs. In an approach[114] similar to that for metal−metal mixed valency, the occurrence of two or more (equivalent) redox-active ligands as in (NIL)−M−(NIL) can lead to interligand electron transfer between differently charged ligands in the excited state (ligand-to-ligand intervalence charge transfer, LLIVCT) or to corresponding dynamics in the ground state (electron hopping). The function of the metal (innocent or noninnocent) is then to provide a scaffold ("coordination") for the interacting ligands and to sometimes participate in the ligand sphere-centered processes. Such elementary studies are based on the significant "reactions of coordinated ligands" for stoichiometric and catalytic conversions.[115]

One aspect pertaining to the occurrence of radical intermediates as ligands like in $(\mathrm{NIL}^{\bullet})$−M−$(\mathrm{NIL}^{\bullet})$ is the observation that some of the resulting even-electron complexes can exhibit a diamagnetic ground state and may thus be referred to as "singlet diradicals".[44b,116,117] Wieghardt, Neese, and associates have presented a detailed description of bis(iminosemiquinone)-nickel(II) species, where the ligands are identified as radicals alone from the structure while the central metal supports the radical−radical interaction.[116] Switching to an odd-electron copper(II) as the central metal, the resulting three-spin interaction within the planar arrangement was analyzed to yield one effective *metal-centered* spin in the ground state (Scheme 7, left).[13] However, a small modification (Scheme 7, right) introducing a potentially coordinating alkylthioether function, which allows for weak (3.2 Å) Cu−S interaction accompanied by a twist of about 32°, caused a qualitative rearrangement of the spin interaction, now resulting in *ligand-centered* spin.[118]

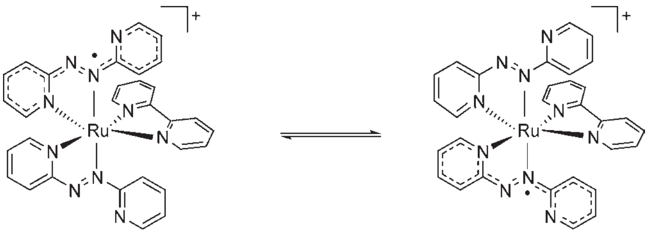
Apart from the conformation-dependent three-spin interaction (Scheme 7), the noninnocent behavior of **16** leads to multiple ligand-centered electron-transfer processes. For instance, upon reduction of $[(\mathbf{16})\mathrm{Cu^{II}}(\mathbf{16})]$, a strongly NIR-absorbing anion $[(\mathbf{16}^{-})\mathrm{Cu^{II}}(\mathbf{16})]^-$ is obtained, with its long-wavelength transition ($\lambda_{\max}$ = 2000 nm) being attributed to an amidophenolato-to-iminosemiquinonato LLIVCT.[118]

The crucial role of coordination stereochemistry for the interaction between NILs is also illustrated by the different temperature-dependent EPR response of one-electron-reduced bis[2,2′-azobis(pyridine)]ruthenium(II) complexes (Scheme 8). EPR line-width broadening as a function of the temperature suggests configuration-dependent spin hopping for the *trans*-azo system **17** in contrast to other configurations involving *cis*-positioned azo groups.[119]

12. INTERACTION POTENTIAL OF DIFFERENT COORDINATED NILs

In nondegenerate cases, i.e., in the presence of at least two *different* NILs, an array of experimental and theoretical methods such as X-ray diffraction, IR/Raman, UV−vis−NIR, EPR/NMR, XAS, and time-dependent DFT is typically advised to establish

Scheme 8. Spin Hopping between Equivalent Redox-Active Ligands[119]



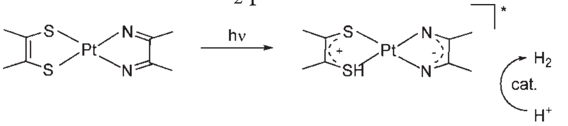
17

the oxidation-state assignments for individual charge states. Examples may involve combinations of NO^n, quinone-type ligands, porphyrins, and other NILs coordinated by, e.g., iron[120] or ruthenium.[121] It was pointed out[5] that such combinations (which include substrates) occur in enzymes, e.g., O_2 and quinones with (heme-)iron or copper in oxidases,[76,77,122] or pterine/dithiolene with M = Mo or W in oxotransferases (Scheme 9).[123]

The acknowledged purpose of such a cooperation is to effect multielectron reactivity,[5] which circumvents the necessity to use platinum element catalysts.[35]

13. NIL BEHAVIOR AND CHARGE-TRANSFER EXCITED STATES

Coordination compounds containing potentially redox-active ligands can support metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMCT), and especially ligand-to-ligand charge-transfer (LLCT) photochemistry. The latter has been demonstrated with planar platinum(II) systems containing dithiolate donors and α-diimine acceptors. The donor → acceptor LLCT in such sensitizer complexes may lead to excited states that can effect H_2 production from water.[124]



(12)

It has been mentioned above that radical-ion-bridged mixed-valent configurations[81,125] such as eq 6 may be viewed as ground-state models for excited states of conventional homovalent compounds (eq 13).

$$\mathrm{Ru^{II}}(\mu\ \text{-}\mathrm{L^0})\mathrm{Ru^{II}} \xrightarrow{\mathrm{MLCT}} [\mathrm{Ru^{2.5}}(\mu\ \text{-}\mathrm{L^{\bullet-}})\mathrm{Ru^{2.5}}]^* \xleftarrow{\mathrm{LMCT}} \mathrm{Ru^{III}}(\mu\ \text{-}\mathrm{L^{2-}})\mathrm{Ru^{III}} \tag{13}$$

Conversely, the excited states of such species resemble conventional homovalent configurations (eq 14).[81b]

$$[\mathrm{Ru^{II}}(\mu\ \text{-}\mathrm{L^0})\mathrm{Ru^{II}}]^* \xleftarrow{\mathrm{LMCT}} [\mathrm{Ru^{2.5}}(\mu\ \text{-}\mathrm{L^{\bullet-}})\mathrm{Ru^{2.5}}]^* \xrightarrow{\mathrm{MLCT}} [\mathrm{Ru^{III}}(\mu\ \text{-}\mathrm{L^{2-}})\mathrm{Ru^{III}}]^* \tag{14}$$

This concept holds also for mononuclear species, e.g., complexes of 2,2′-bipyridine (bpy) with the very strongly π-donating organometal complex fragments $M(C_nR_n)$, where M = Rh and Ir and $n = 5$ or M = Ru and Os and $n = 6$. The acceptance of an electron equivalent by the otherwise less strongly π-accepting bpy NIL leads characteristically to an unusual *cathodic* shift of the reduction potential of the product, signifying the dominant metal-to-ligand flow of negative charge versus the conventional ligand-to-metal coordinative bonding.[17] Accordingly, the spectroscopic signature of a vibrationally structured NIR band for $bpy^{\bullet-}$ is observed,[17] and the formulation, e.g., for **18**, corresponds to the excited-state description of a conventional complex like **19**.[126]

$$\underset{\mathbf{18}}{[\mathrm{Rh^{II}}(\mathrm{bpy^{\bullet-}})(\mathrm{C_5Me_5})]} \tag{15}$$

$$\underset{\mathbf{19}}{[\mathrm{Rh^{I}}(\mathrm{bpy})(\mathrm{dio})]} \xrightarrow[h\nu]{\mathrm{MLCT}} [\mathrm{Rh^{II}}(\mathrm{bpy^{\bullet-}})(\mathrm{dio})]^* \tag{16}$$

where dio = diolefin, e.g., 1,5-cyclooctadiene or 2,5-norbornadiene.

The results obtained from combining very strongly π-donating organometallic fragments $M(C_5Me_5)$, where M = Rh, Ir, and α-diimine acceptors (dab and bpy),[17b,c] illustrate how charge transfer, one-electron and even two-electron transfer from the metal to the ligand, can occur within a related class of molecules. The strongest[17] π donor $Ir(C_5Me_5)$ and a strong π acceptor [a 1,4-bis(2,6-dimethylphenyl)-substituted 1,4-diazabuta-1,3-diene, dmp-dab] thus form a chelate complex clearly identified as $Ir^{III}(C_5Me_5)(\text{dmp-dab}^{2-})$,[127] where NIL = dmp-dab has used the full capacity to add two electrons. Compounds $M(C_5Me_5)$-(bpy), where M = Rh and Ir, are thus best described as spin—spin-coupled metal(II)/($bpy^{\bullet-}$) species.[17] Recently, a corresponding formulation $Rh^{II}(phdi^{\bullet-})$ was proposed[128] for a rhodium complex of 9,10-phenanthrenediimine (phdi), another member of the α-diimine NIL family. In agreement with earlier assignments[129] for $[Rh^{II}(C_5Me_5)(abpy^{2-})]^-$, the one-electron addition to the Rh(phdi) complex was interpreted[128] as leading to a $Rh^{II}(phdi^{2-})$ situation.

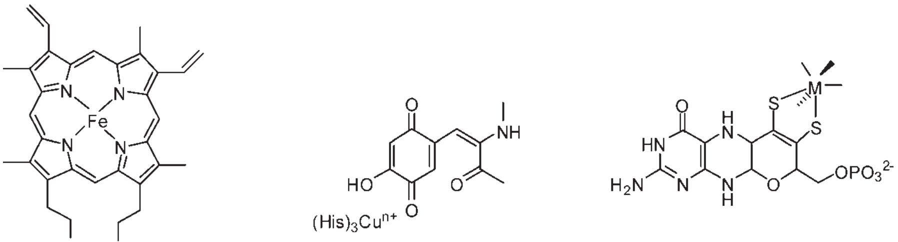
14. USES OF NIL REACTIVITY

Potential applications of complexes with noninnocently behaving ligands in materials science have largely focused on functionalities relevant for information processing. This includes low- and high-molecular-weight coordination compounds with low-energy electronic transitions and corresponding absorptivity in the visible and NIR regions,[99] where radiation harvesting and modulation is an important issue.[103] Other potentials for applications rely on the spin information associated with radical intermediate ligands, which can be employed in metal/ligand spin-interaction arrangements of varying complexity (see Scheme 7) or in spin-crossover effects involving valence tautomerism.[70c,71]

The potential of NILs for controlling chemical reactions includes (i) the facilitation of single-electron-transfer reactivity, e.g., for enhancing selective bond activation (especially in organometallic chemistry),[34,38,114,130] (ii) the electron accumulator and reservoir function for multielectron processes,[35,131] especially converting small molecules with high activation requirements ("Radical Ligands Confer Nobility on Base-Metal Catalysts"[35]), (iii) and an electron buffer capacity for reactivity tuning via fractional electron-density shifts ("δ")[84,85] without involving unusual, high-energy metal oxidation states.

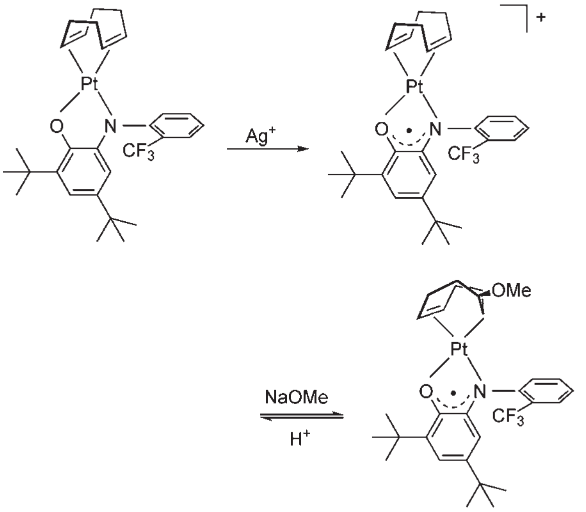
The latter has been illustrated nicely in recent work by Rauchfuss and co-workers by the example of an enhanced nucleophilic attack of RO^- on olefins (eq 17)[132] and by electron-transfer-activated coordination and splitting of H_2, mimicking hydrogenase activity.[36,87a] Complementing this last example (eq 18), the indirect effect of an NIL on the coordinative requirement of a transition metal has been illustrated by analysis

Scheme 9. Functional Transition Metal/NIL Combinations from Biology[5]



M = Mo or W

of the reversible intramolecular one-electron "pseudo-oxidative addition/reductive elimination" equilibrium (19).[87b]



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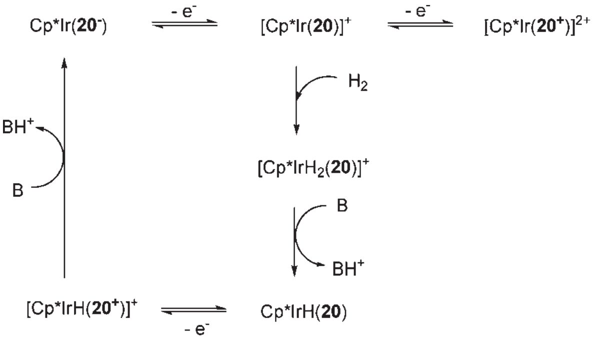

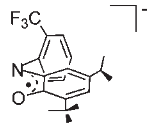

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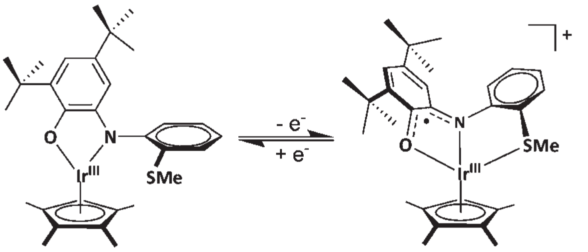
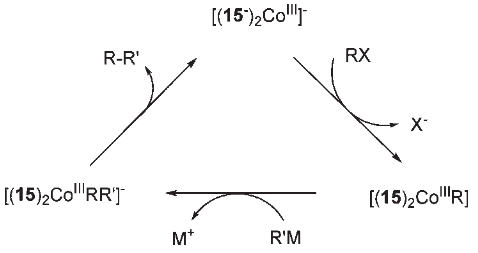


(19)

Equilibrium (19) illustrates the potential of *hemilabile NILs* such as **16**. Reversible weak metal coordination of specific donors in multidentate ligands can thus depend not only on the oxidation state of the metal (see Scheme 7)[118] but also on the oxidation state of the NIL. In addition to copper and iridium,[87b] other transition metals such as Ni, Co, Rh, Ru, Os, Pd, and Pt were shown to form redox-active complexes with the hemilabile **16**.[133]

The electron capacity of redox-active ligands, especially of quinone-type species such as 4,6-di-*tert*.-butyl-*N*-aryl-*o*-iminobenzosemiquinonato (**15**),[134] has been used to effect element—element bond formation (eqs 20 and 21).[1c,135]

$$(\mathbf{15}^{-})_2\mathrm{Zr^{IV}(solv)_2} + \mathrm{X_2} \xrightarrow[\mathrm{X\,=\,Ph^{134b}}]{\mathrm{X\,=\,Cl^{134a}}} (\mathbf{15})_2\mathrm{Zr^{IV}X_2} \xleftarrow{-\,2\,e^-} \left[(\mathbf{15}^{-})_2\mathrm{Zr^{IV}X_2}\right]^{2-} \qquad (20)$$



(21)

As in example (19),[87b] the metal oxidation state remains virtually unchanged, and the NIL-supported conversion (21) is thus referred to as a two-electron "pseudo-oxidative addition/reductive elimination".[1c]

15. CONCLUDING REMARKS

This article is an attempt to present an overview of several phenomena that can occur only in the presence of redox-active, noninnocently behaving ligands. The various aspects and situations include the establishment of oxidation states, the identification of radical ligands, the physical and chemical consequences of ligand redox reactions, and several ambivalent situations such as the delocalized "resonance" case versus valence tautomer equilibria, or dinuclear radical-bridged systems versus the mixed-valent alternative. Additional complexity may result for NIL-bridged coordination compounds of higher nuclearity and for systems with more than one noninnocently behaving ligand (ligand-based mixed valency, stereochemical aspects, and spin—spin coupling). Excited states and dynamic processes add further dimensions. Not only does the electron-transfer activity of redox-active ligands touch fundamentally significant aspects, it can also create functionality of the resulting coordination compounds in terms of attractive material properties and interesting reactivity involving controlled radical activity and electron reservoir behavior. This aspect is all the more important because the scope of potentially redox-active ligands is continuously being extended beyond the better-established systems (cf. Scheme 1) to produce unusual new species such as $NO^{\bullet 2-}$ or $CO_2^{\bullet -}$[47,48,136] or to reveal "hidden"[137] noninnocence of typically innocent kinds of molecules.

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