Mixed Valence
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Unconventional Mixed-Valent Complexes of Ruthenium and Osmium

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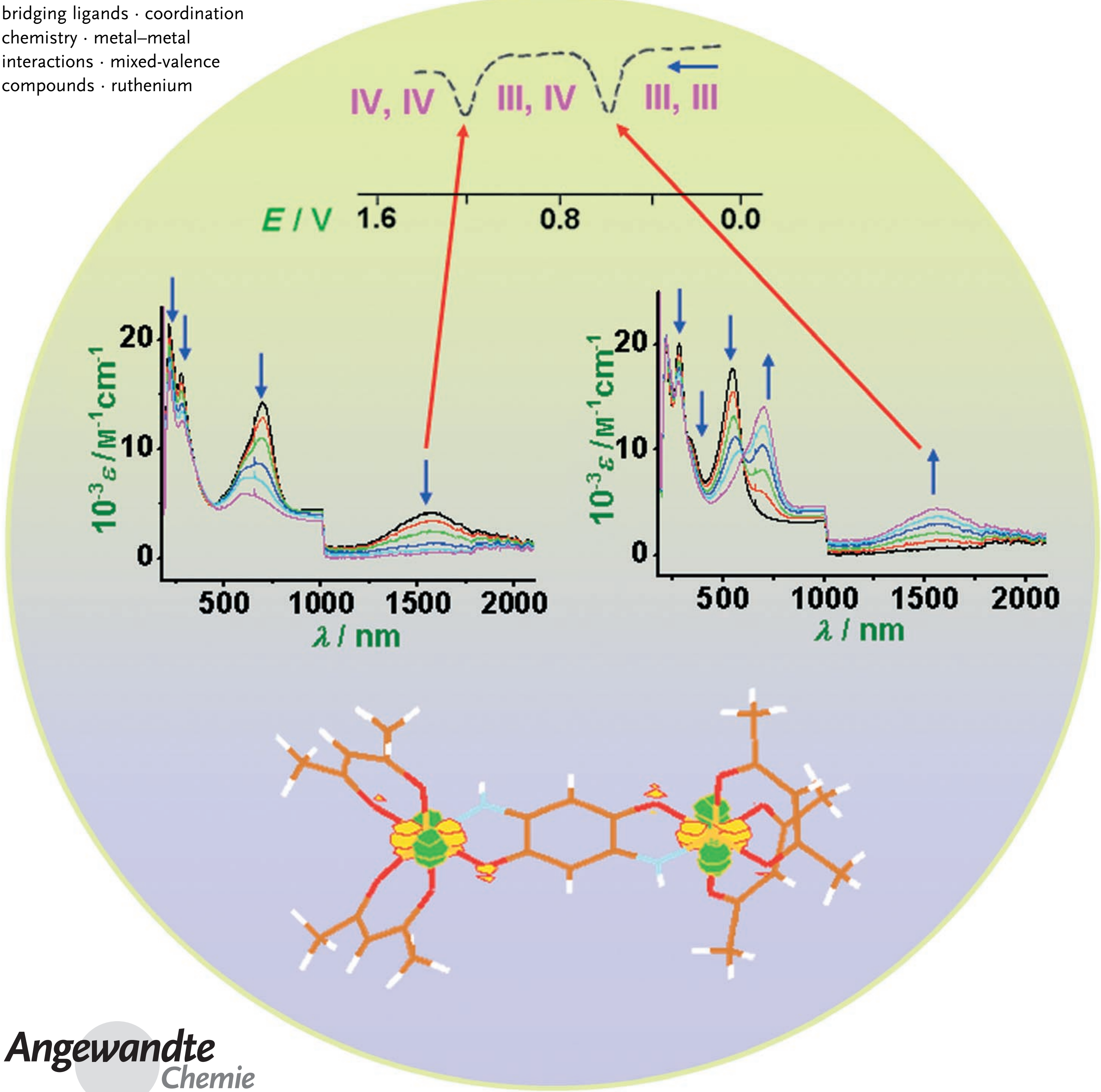
bridging ligands · coordination chemistry · metal–metal interactions · mixed-valence compounds · ruthenium

In memory of Henry Taube (1915–2005)



Recent developments have helped to extend the repertoire of mixed-valent ruthenium and osmium complexes beyond conventional systems. This extension has been achieved by using sophisticated ligands and by creating more variegated coordination patterns. The strategies employed include the use of multidentate ligands (which give rise to multinuclear and chelate complexes) and the use several redox active components (non-innocent ligands and oxidation-state ambivalence). The results offer enhanced chemical insight into metal–ligand electron-transfer situations and suggest that mixed-valent materials may eventually be exploited in molecular electronics and molecular computing.

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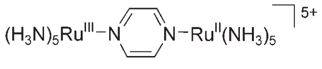
1. Introduction

1.1. Mixed Valence

The concept of valence—having fallen into disrepute at times even in Inorganic Chemistry—has recently made a strong comeback, based on the competent and ingenious application of the available array of modern physical methods.[1] Within that concept, "mixed valence"[2,3] is a ubiquitous phenomenon with examples ranging from the smallest conceivable (ionic) molecule, H_2^+ with a hydrogen oxidation state of 0.5, to coordination polymers, such as Prussian Blue, $Fe_4[Fe(CN)_6]_3$ (oxidation states Fe^{III} and Fe^{II}). There are also several naturally occurring mixed-valence entities from the geo- and biosphere, such as Fe_3O_4 (magnetite) or $\{(Cys)_2Fe^{II}(\mu\text{-}S)_2Fe^{III}(Cys)_2\}$ ($[2Fe\text{-}2S]^+$ centers in proteins). The examples involving the $Fe^{III}Fe^{II}$ combination already illustrate the prevalence and stability of the d^5/d^6 configuration.

Ruthenium, the heavier homologue of iron, has also been of great significance for the field of mixed-valence chemistry owing to the thermodynamic and kinetic stability of the neighboring oxidation states Ru^{III} and Ru^{II};[4] textbook examples include metal–metal bonded systems,[5] atom- and molecule-bridged species, such as the Creutz–Taube ion **1**,[6,7] and organometallic compounds.[8,9]



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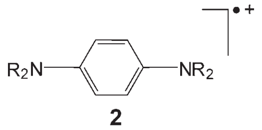
Following the rapid expansion of the field there are now several leading reviews available for conventional, that is, dinuclear $Ru^{III}Ru^{II}$ compounds $[L_xRu^{III}(\mu\text{-BL})Ru^{II}L_x]$ (where μ-BL is a bridging ligand) with largely innocent, not obviously redox-active bridging ligands.[10–18] The interest in these compounds was originally fostered by their function as test systems for experimental and theoretical studies of electron transfer.[4,13,19] Later, the focus shifted to the use of advanced spectroscopic methods, such as resonance Raman or Stark spectroscopy,[20] and to the application potential of mixed-valent systems in general for molecular electronics (wires,[15,16,21,22a,b] switches,[16,22a,c] quantum cellular automata, molecular computing;[23,24] see Section 2.12).

Furthermore, the concept of bridge-mediated mixed-valence has been successfully extended to organic and main-group element compounds involving for example, oxidizable diamines,[25a b] such as the colored Wurster's salts **2** or reducible π-bridged diboranes, such as **3**.[25c]



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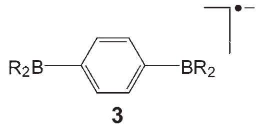

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1.2. Standard Characterization Methods for Mixed-Valent Systems

1.2.1. The Comproportionation Constant

For two-step redox systems in solution, one of the most essential parameter is the comproportionation constant K_c as obtained from electrochemical potential differences, for example, through polarography, cyclic voltammetry, or differential pulse voltammetry.[10–12,18] Equations (1) and (2) illustrate the relevant equilibria by example of ligand-bridged (μ-BL) metal complex fragments $\{L_xM^{n/n+1}\}$ (L: ancillary terminal ligands).

$$\underset{\text{Red}}{[L_xM^n(\mu\text{-BL})M^nL_x]} \underset{(E_1)}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} \underset{\text{Int}}{[L_xM^n(\mu\text{-BL})M^{n+1}L_x]} \underset{(E_2)}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} \underset{\text{Ox}}{[L_xM^{n+1}(\mu\text{-BL})M^{n+1}L_x]} \qquad (1)$$

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$$K_c = \frac{[\mathrm{Int}]^2}{[\mathrm{Red}][\mathrm{Ox}]} = 10^{\Delta E/59\,\mathrm{mV}} \quad \text{at } 298\,\mathrm{K} \qquad (2)$$
$$\Delta E = E_2 - E_1;\; RT\ln K_c = nF\Delta E$$

K_c is a complex quantity, with the free energy ΔG_c of comproportionation depending very much on the electrolyte environment;[26] according to Equation (3), ΔG_c is made up from several contributions.[12,27] In case of small K_c values the presence of the neighboring redox states in the equilibrium has to be considered which may require a correction by concentration-dependent spectroscopic measurements.[28]

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{af} + \Delta G_{ip} \qquad (3)$$

In Equation (3)[12,27] ΔG_s represents the statistical distribution, ΔG_e the electrostatic repulsion of the positively charged metal ions, ΔG_i an inductive factor related to the competitive coordination of the bridging ligand by the metal ions, ΔG_r the resonance exchange, ΔG_{af} the antiferromagnetic exchange stabilization, for example, of the $M^{III}M^{III}$ state over its mixed-valent form, and ΔG_{ip} the ion-pairing effects depending on the charges of the complexes.

In this context it may be noted that the use of the confusing term "coupling" is discouraged for mixed-valent systems because it may be used to describe a stability constant from electrochemical measurements (K_c), an electronic interaction parameter (V_{ab}), or magnetic exchange phenomena (J). Also, an equilibrium constant K_c for an intermediate does not by itself prove the mixed-valence character of that intermediate (**A** in Equation 4); valence-averaging (**B** in Equation 4) or the partial or even complete involvement of the ligand as the electron-transfer site (**C** in Equation 4) have to be considered. The support of, for example, electrochemically determined equilibrium constants by spectroscopic identification ("spectroelectrochemistry") has thus become a very useful practice in mixed-valence research, as illustrated throughout this article.

$[L_xM^n(\mu\text{-BL})M^{n+1}L_x]$
A, localized mixed valence

$[L_xM^{n+0.5}(\mu\text{-BL})M^{n+0.5}L_x]$
B, delocalized mixed valence (4)

$[L_xM^n(\mu\text{-BL}^{\bullet+})M^nL_x]$
C, radical complex

1.2.2. The Electronic Interaction Energy

Frequently, the intervalence charge-transfer (IVCT) absorption bands have been recognized as the most conspicuous evidence for a mixed-valent situation. They arise from intramolecular electronic transitions [Eq. (5a,5b)] from electron-rich lower-valent to electron-deficient higher-valent sites.[2,14] The corresponding bands from absorption spectroscopy in the visible (e.g. for Prussian Blue) or in the near-infrared region (e.g. at 1570 nm for the Creutz–Taube ion,[6] see also Figure 1) may be asymmetrical or structured and may have very different intensities which can create technical problems owing to the lower sensitivity of detectors in the near-infrared region.

$$[L_xM^n(\mu\text{-BL})M^{n+1}L_x] \xrightarrow[\mathrm{IVCT}]{h\nu} {}^*[L_xM^{n+1}(\mu\text{-BL})M^nL_x] \qquad (5a)$$

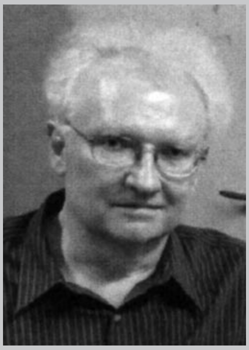
$$[L_xM^{n+0.5}(\mu\text{-BL})M^{n+0.5}L_x] \xrightarrow[\mathrm{IVCT}]{h\nu} {}^*[L_xM^{n+0.5}(\mu\text{-BL})M^{n+0.5}L_x] \qquad (5b)$$

The interest in IVCT bands, in their energies, intensities, band shapes and widths, stems from their close, if not always straightforward, connection with of the electronic interaction.[17–19] In the classical limit, the bandwidth at half height ($\Delta\nu_{1/2}$) is related to the energy maximum (E_{max}) according to the Hush equation [Eq. (6)].[19a] Following Hush, the electronic coupling energy V_{ab} as reflected by the IVCT parameters of a symmetrical band is given by Equation (7) where

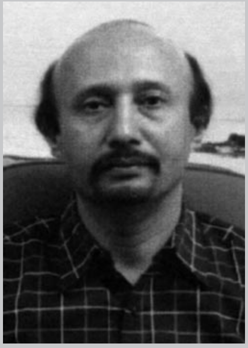
$$\Delta\nu_{1/2} = [2.31 \times 10^3\ (E_{max})]^{1/2} \qquad (6)$$

$$V_{ab} = \{[2.05 \times 10^{-2}(\varepsilon_{max}\bar{\nu}_{max}\bar{\nu}_{1/2})^{1/2}]/R\} \qquad (7)$$

ε_{max}, $\bar{\nu}_{max}$ and $\bar{\nu}_{1/2}$ are the molar extinction coeffients, the absorption maximum in wavenumbers, and the bandwidth at half height in wavenumbers, respectively; R is the metal–metal distance in Å for a valence-localized situation.[19a] For a fully delocalized case,[19b] V_{ab} amounts to $\bar{\nu}_{max}/2$. Introducing superexchange concepts, Creutz, Newton, and Sutin have later extended the model to allow the use of metal–ligand charge-transfer energies.[19c] Approaches including more than one state have been put forward more recently.[13]



Wolfgang Kaim received the Dr. Phil. Nat. degree from Frankfurt/Main, Germany, in 1978 and spent a postdoctoral year with F. A. Cotton at Texas A& M University. Since 1987 he has held the chair in coordination chemistry at the University of Stuttgart. His research, listed in about 500 publications, deals with chemical and spectroscopic manifestations of electron transfer and with the characterization of unusual redox states in newly synthesized molecules.



Goutam Kumar Lahiri received his Ph.D. from the Indian Association for the Cultivation of Science in Kolkata, India, in 1990. After postdoctoral work with A. M. Stolzenberg at the University of West Virginia, USA, he joined the Indian Institute of Technology Bombay where is a professor. He has been elected Fellow of the Indian Academy of Sciences, Bangalore and is the recipient of B. M. Birla award in Chemistry. His work primarily focuses on synthesis, reactivity studies, electron-transfer aspects, and catalysis of transition-metal complexes.

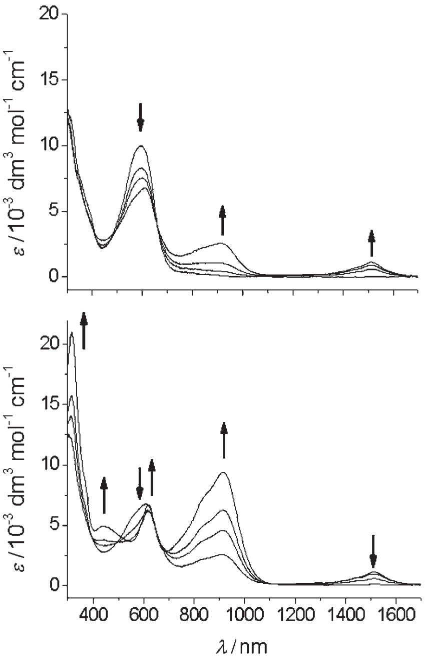


Figure 1. Spectroelectrochemical changes on going from $[(Cym)Ru^{0}(\mu\text{-abpy})Ru^{II}Cl(Cym)]^{+}$ to $[(Cym)Ru^{I}(\mu\text{-abpy}^{2-})Ru^{II}(Cym)]^{+}$ (top) and from $[(Cym)Ru^{I}(\mu\text{-abpy}^{2-})Ru^{II}(Cym)]^{+}$ to $[(Cym)Ru(\mu\text{-abpy})Ru(Cym)]$ (bottom) in CH_3CN/0.1 M Bu_4NPF_6 (Cym = η^6-*p*-cymene, abpy = 2,2′-azobispyridine). The intervalence charge-transfer band around 1500 nm in the near-infrared region occurs only for the mixed-valent intermediate.

1.2.3. *Information from Vibrational Spectroscopy*

An increasingly useful method to study mixed-valent compounds is vibrational spectroscopy (IR, Raman) which yields not only information on molecular symmetry but also allows indirect rate estimates within a very fast time frame of picoseconds for intramolecular electron transfers (see Section 2.13).[29] The essential question of time scale[14,30] in mixed-valence chemistry will be addressed in following sections.

1.2.4. *Information from Electron Spin*

Since most mixed-valent systems are paramagnetic, the interaction and resonance properties of electron spins determined from susceptibility or EPR measurements (*g*-factor effects, hyperfine splitting)[3b,16b,31] can be used to determine "physical" oxidation states.[1] Alternative methods are X-ray photoelectron or X-ray absorption spectroscopy (XPS, XAS) or Mössbauer spectroscopy, if applicable.

1.3. *Scope of the Review*

The scope of this article is restricted to symmetrical molecular ligand-bridged mixed-valence compounds with a capability of ligand-mediated degenerate intramolecular electron transfer (valence exchange). We thus deal with indirect metal–metal interactions whereby the mediator function of the typically organic bridging ligand is highly variable. Directly M–M bonded systems[5] or atom-bridged species[5,32] are not considered; relative to the overwhelming number of reports on ruthenium compounds[8–18] the number of studies with osmium has been rather small.[14,17b]

1.4. *New Developments: An Overview*

The conventional type[33] of ligand-bridged diruthenium mixed-valent complexes as dealt with in typical review articles[10–18] can be summarized as follows: It is a usually dinuclear M^{II}/M^{III} complex with simple, apparently redox-innocent ancillary ligands (L) and bridging ligands (BL). Its straightforward classification following the Robin and Day scheme[2] (see Section 2.11) is based on mostly parallel electrochemical and optical-spectroscopic manifestations of metal–metal interaction and on the metal–metal distance.

In this article we present examples of recent developments which go beyond the conventional pattern. The following new aspects will be addressed:

- the involvement of less-common oxidation states, such as +IV (d^4) or +I (d^7) for ruthenium,
- higher nuclearity (tri-, tetra-, hexanuclear systems),
- the use of functional bridges,
- the advantages of mixed donor–acceptor bridges,
- non-innocent bridges, potentially functioning as radicals,
- strongly donating or accepting ancillary terminal ligands,
- effects of varying the coordinating (donor) atoms,
- new aspects of the differences between ruthenium and osmium complexes,
- strongly divergent electronic and electrostatic "coupling",
- the role of the metal–ligand interface in addition to mere distance effects,
- the occurrence of "Class II/III borderline" mixed-valence systems and the case for abandoning the Robin/Day classification,
- the potential for molecular wiring, switching, and computing in molecular electronics,
- facile access to the study of ultrafast dynamics.

2. *Unconventional Mixed-Valent Systems*

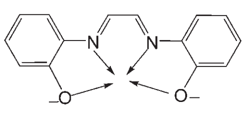
2.1. *Involvement of Unusual Oxidation States*

The vast majority of stable mixed-valent species contain metal centers in the d^5/d^6 configuration, especially in the $Fe^{III}Fe^{II}$ and $Ru^{III}Ru^{II}$ combinations.[2,3a,8–18] There have been far fewer reports of complexes with the more unusual ruthenium oxidation state +IV (d^4) which requires strongly electron-donating ligands, such as oxide, cyanamides, phenolates, or acetylacetonate ($acac^-$).[27,34–37]

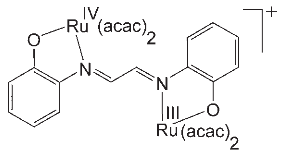
The higher oxidation states +III and +IV imply an increased covalency of the metal–donor bond which limits the usefulness of the valence description. Frequently, the donor bridges involved are thus "non-innocent" so that alternatives according to the resonance formulation [Eq. (8)] can be proposed.

$$\{\mathrm{Ru^{IV}}(\mu\text{-}\mathrm{BL^{2-}})\mathrm{Ru^{III}}\} \leftrightarrow \{\mathrm{Ru^{III}}(\mu\text{-}\mathrm{BL})\mathrm{Ru^{II}}\} \tag{8}$$

Two such examples[36,37] are **4** and **5** which were obtained by oxidation of well-characterized $\mathrm{Ru^{III}Ru^{III}}$ precursors and which illustrate how different kinds of mixed-valent intermediates can be encountered. The dianion of glyoxalbis(2-hydroxyanil) ($\mathrm{gbha^{2-}}$) is an established analytical color reagent for the quantitative determination of large metal ions, such as $\mathrm{Ca^{2+}}$ or $\mathrm{Pb^{2+}}$, acting as tetradentate pseudomacrochelate ligand. However, with $[(\mathrm{acac})_2\mathrm{Ru}]^{n+}$ the potentially four-step redox system gbha^{k-}, $k = 0$–4,[36] forms dinuclear complexes in which it acts as a bis-bidentate chelating ligand. These complexes can undergo a series of electron-transfer processes during which an oxidized odd-electron cation $[(\mu\text{-gbha})\{\mathrm{Ru(acac)_2}\}_2]^+$ (**4**) with $K_c = 10^{6.2}$, $\lambda_{\max} = 1795$ nm ($\varepsilon = 2500\,\mathrm{M^{-1}cm^{-1}}$), and $g_\perp = 2.220$; $g_\parallel = 1.805$ as EPR signature is formed.



$\mathrm{gbha^{2-}}$



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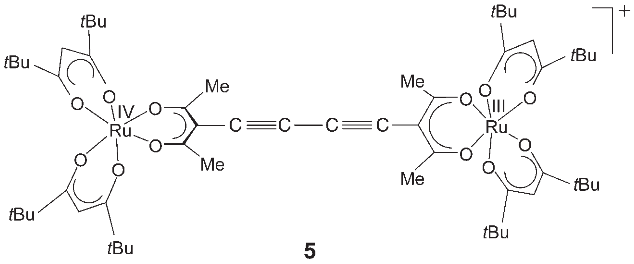

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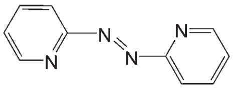
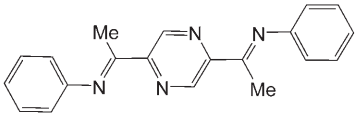
The bridging ligand in complex **5** contains two electron-rich Werner-type coordination sites for ruthenium. The metal centers are 13.1 Å apart in the neutral $(\mathrm{Ru^{III}})_2$ form, and are connected through an approximately linear $\mathrm{C_4}$ chain. The one-electron oxidation to **5** ($K_c = 10^{3.8}$) does not only cause the emergence of an intense near-infrared band at 1730 nm but also a shift to lower energy and strong increase in the intensity of the IR stretching band of the $\mathrm{C_4}$ backbone.[37] The unusual IR features were attributed to cumulene-type resonance contributions.[37] The $\mathrm{Ru^{IV}Ru^{III}}$ mixed-valent intermediates may exhibit different spin states owing to the $\mathrm{d^5/d^4}$ ($S = {}^1\!/_2/S = 1$) configuration, a situation also observed with $\mathrm{Fe^{IV}Fe^{III}}$.[38]

Combinations involving oxidation states lower than the classical +III/+II combination, such as ruthenium(I),[39] typically require stabilization through organometallic π-acceptor ligands. Organometallic $\mathrm{Ru^{III}Ru^{II}}$ compounds have long been established.[8,9] Very recently, however, the thorough investigation of the stepwise reduction behavior of acceptor-bridged dinuclear arene ruthenium(II) complexes $[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)Cl}\}_2]^{2+}$, (BL = 2,2′-azobispyridine (abpy)[40a] or 2,5-bis(1-phenyliminoethyl)pyrazine (bpip)),[40b] has shown[41] the formation of radical complexes after one-electron addition, chloride loss after the second electron addition, and the formation of three-electron reduction products which are characterized experimentally (Figure 1)[41a] and computationally (Figure 2)[41b] as mixed-valent intermediates $\{(\mu\text{-BL})[\mathrm{Ru(C_6R_6)}]_2\}^+$ (Scheme 1). Although the EPR (g anisotropy) and absorption data (near-infrared band, Figure 1) confirm the calculated mixed-valent character with the $\{\mathrm{Ru^{II}}(\mu\text{-}\mathrm{BL^{2-}})\mathrm{Ru^{I}}\}$ description as the most appropriate formulation for BL = abpy, the very small comproportionation constants of about 10^2 reflect the involvement of a $\mathrm{d_\sigma}$ electron (from the e_g sub-set) instead of a $\mathrm{d_\pi}$ electron (from the t_{2g} sub-set) in the electron exchange between $\mathrm{Ru^I}$ ($\mathrm{d^7}$) and $\mathrm{Ru^{II}}$ ($\mathrm{d^6}$).



abpy



bpip

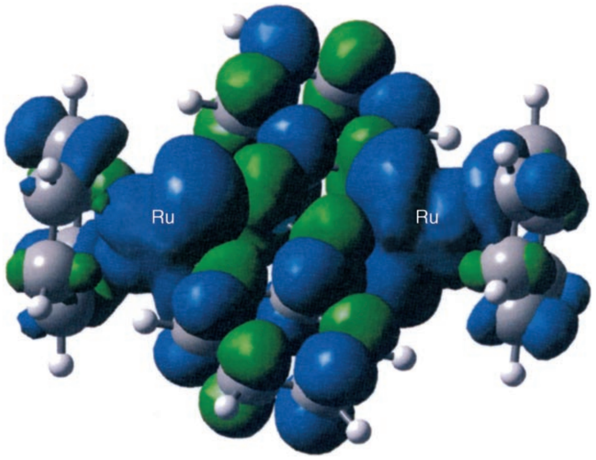


Figure 2. DFT calculated spin densities for $[(\mu\text{-abpy})\{\mathrm{Ru(C_6H_6)}\}_2]^+$, illustrating the largely metal-centered spin in a $\mathrm{Ru^{1.5}}_2$ situation. The blue and green areas correspond to the regions of positive and negative spin density, respectively.

$$\begin{tikzcd}[row sep=large]
{[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)Cl}\}_2]^{2+}} \arrow[d, shift left, "+\,e^-"] \\
{[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)Cl}\}_2]^{+}} \arrow[u, shift left] \arrow[d, shift left, "+\,e^-,\,-Cl^-"] \\
{[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)Cl}\}\{\mathrm{Ru(C_6R_6)}\}]^{+}} \arrow[u, shift left] \arrow[d, shift left, "+\,e^-,\,-Cl^-"] \\
{[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)}\}_2]^{+}} \arrow[u, shift left] \arrow[d, shift left, "+\,e^-"] \\
{[(\mu\text{-BL})\{\mathrm{Ru(C_6R_6)}\}_2]} \arrow[u, shift left]
\end{tikzcd}$$

Scheme 1.

DFT calculations for the paramagnetic intermediates [(μ-abpy){Ru(C_6H_6)Cl}$_2$]$^+$ and [(μ-abpy){Ru(C_6H_6)}$_2$]$^+$ (Figure 2) confirm the notion of an {(abpy$^{\bullet-}$)Ru_2^{II}} formulation in the former intermediate and a description {(abpy^{2-})$Ru_2^{1.5}$} for the latter, chloride-free cation.[41b]

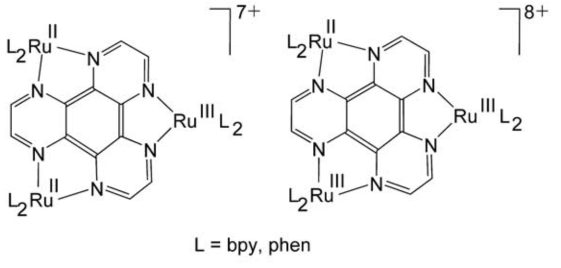
Dinuclear organometallic complexes with d^7 configured metal centers have been described with Rh^{II}, Ir^{II}, and Pt^{III}.[42] In contrast to metal–metal linked oligomers, such as Pt^{II+x} (d_{z^2} orbitals[43]), small K_c values were always observed with π-conjugated bridging ligands,[41,42] in agreement with the above argument.

2.2. Nuclearity Higher than Two

2.2.1. Trinuclear Systems

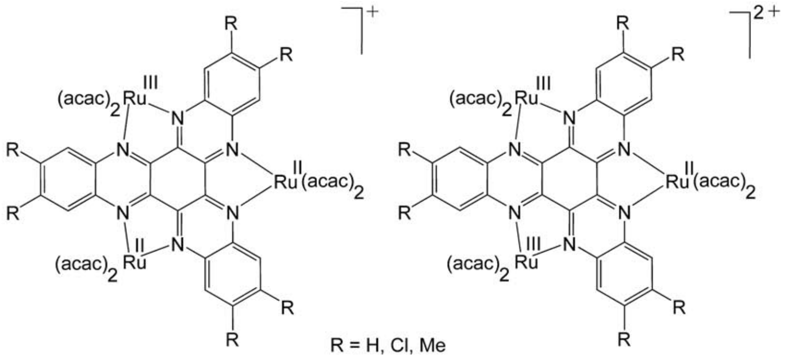
In contrast to the vast number of mixed-valent ligand-bridged diruthenium complexes[8–18] there have been relatively few reports or reviews[17b] on related symmetrical trinuclear compounds.[44–47] If the common Ru^{III}/Ru^{II} pairs are involved, this arrangement can lead to two different mixed-valent states, $Ru^{III}Ru^{II}Ru^{II}$ and $Ru^{III}Ru^{III}Ru^{II}$. A number of such cases have been reported, as is illustrated by the complexes **6**–**9** (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, pap = 2′-phenylazopyridine) and in Table 1.[44–47]

In the cases from Table 1 both different mixed-valent combinations were accessible as evident from the corresponding K_c values. However, the relative magnitudes of K_{c1} and K_{c2} show considerable variation, depending on the relative stabilities of the Ru^{II} or Ru^{III} states and possibly the valence and spin interaction in the $Ru^{III}Ru^{III}Ru^{II}$ state. Even seemingly simple substitution at the periphery in complexes [(μ_3-BL){Ru(acac)$_2$}$_3$] (**7**; BL = substituted diquinoxaline[2,3-*a*;2′,3′-*c*]phenazines), showed qualitative variations in K_c values (Table 1).[46] The $Ru^{III}Ru^{II}Ru^{II}$ form could be characterized by EPR spectroscopy. For **6** which has the



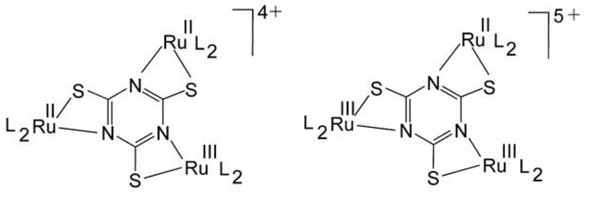
L = bpy, phen

6



R = H, Cl, Me

7



L = bpy, phen, pap

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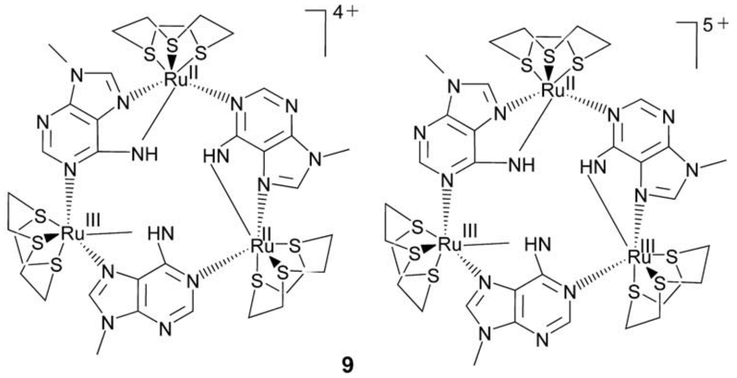

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Table 1: Mixed-valent triruthenium complexes.

Complex	Ref.	K_{c1}[a]	K_{c2}[a]	IVCT$_1$[b] λ [nm] (ε [$M^{-1}cm^{-1}$])	IVCT$_2$[b] λ [nm] (ε [$M^{-1}cm^{-1}$])
7, R = H	[46a]	$10^{5.7}$	$10^{8.1}$	[c]	[c]
7, R = Cl	[46b]	$10^{6.8}$	$10^{3.9}$	[c]	[c]
7, R = Me	[46b]	$10^{6.8}$	$10^{3.6}$	[c]	[c]
Δ_3/Λ_3-**6**, L = bpy	[45b]	$10^{3.9}$	$10^{4.1}$	2150 (3315)	2132 (2990)
$\Delta_2\Lambda/\Lambda_2\Delta$-**6**, L = bpy	[45b]	$10^{3.7}$	$10^{4.1}$	2155 (4180)	2036 (2150)
8, L = bpy	[44b]	$10^{3.7}$	$10^{4.1}$	1900 (2300)	1900 (2400)
9	[47a]	$10^{3.0}$	$10^{6.4}$	950 (2950)	2085 (8400)

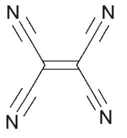
[a] K_c: comproportionation constants for $Ru^{III,II,II}_3$ (K_{c1}) and $Ru^{III,III,II}_3$ (K_{c2}). [b] IVCT: intervalence charge-transfer transitions for the $Ru_3^{II,II,III}$ (IVCT$_1$) and $Ru_3^{II,III,III}$ states (IVCT$_2$). [c] Not observed.

1,4,5,8,9,12-hexaazatriphenylene (HAT) bridging ligand and L = phen[45a], and the related system **7** no IVCT absorption bands were found in the near infrared region[46], whereas the analogous intermediates **6** with L = bpy were recently reported to exhibit such bands at around 2000 nm.[45b] The $Ru^{III}Ru^{II}Ru^{II}$ and $Ru^{III}Ru^{III}Ru^{II}$ intermediates may differ substantially in their K_c values and valence (de)localization.[46,47a]

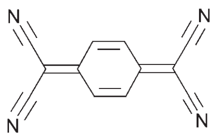
Following the pioneering work by Taube and co-workers from 1978[48a] there have been also a number of reports on mixed-valent triruthenium complexes, such as $[L_nRu\{(\mu\text{-}BL)RuL'_k\}_2]$ μ-BL = CN^-, pyrazine, 4-cyanopyridine, with the inequivalent metal centers in different coordinative environments.[48]

2.2.2. *Tetranuclear Systems*

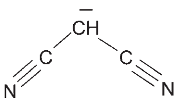
Tetraruthenium mixed-valent complexes[17b] have been described[49] in the form of systems $[(\mu_4\text{-TCNX})\{Ru(NH_3)_5\}_4]^{8+}$ where the bridging ligands TCNX exist as non-planar dianions $TCNE^{2-}$ or $TCNQ^{2-}$, leaving averaged $Ru^{2.5}$ oxidation states for the four equivalent metal centers. This "dimer of mixed-valent dimers" model is supported by electrochemistry, spectroscopy,[49a] magnetism,[49b] and by recent DFT calculations;[49c] the strongly coupled diruthenium(III,II) entities contain the well-known bis-monodentate malonodintrilato (mdn^-) donor bridge,[50] and are directly linked (in the TCNE system) or bridged by a *p*-phenylene unit (in the TCNQ analogue). Remarkably, the mixed valency disappears both on oxidation (two-electron oxidation to the $\{(TCNX^{2-})(Ru^{III})_4\}$ configuration) and on one-electron reduction (formation of $\{(TCNX^{\bullet-})(Ru^{II})_4\}$, spectroscopically demonstrated).[49]



TCNE



TCNQ



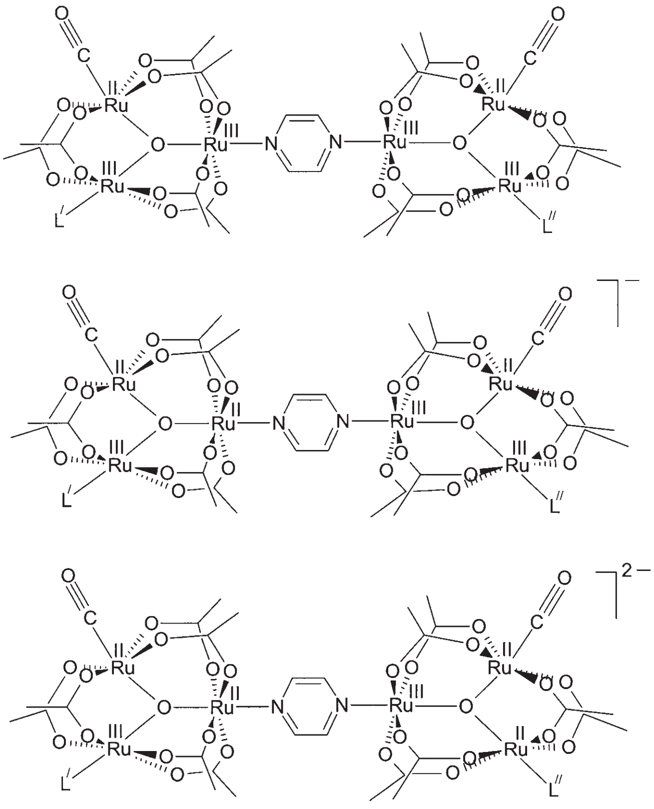
mdn^-

A molecular square $[\{(\mu\text{-pz})Ru(cyclen)\}_4]^{9+}$ (pz = pyrazine, cyclen = 1,4,7,10-tetraazacyclododecane), which is related to the Creutz–Taube ion has been crystallized for X-ray structure analysis, however, the electrochemical and spectroscopic characterization proved difficult.[51] Such squares and the $\{(\mu\text{-TCNE})Ru_4\}$-containing redox system have been considered as models for molecular computing.[24a]

Unsymmetrical mixed-valent tetraruthenium complexes of the type $[Ru\{(\mu\text{-BL})RuL_n\}_3]$ (where μ-BL is a bis(bidentate) bridging ligand), have been obtained by Haga et al. as rudimentary dendritic systems and were analyzed with respect to intervalence charge transfer and response to (de)protonation (see Sections 2.3 and 2.12).[52]

2.2.3. *Hexanuclear Systems*

In a similar fashion to the tetranuclear complexes of TCNE and TCNQ, the hexanuclear species $\mathbf{10}^{n-}$ (in which L′, L″, L‴ are substituted pyridines) are composed from two linked mixed-valent moieties, in this case trinuclear clusters.[47b–d] The oxidation states involved range from $Ru^{III}Ru^{III}Ru^{II}/Ru^{III}Ru^{III}Ru^{II}$ through $Ru^{III}Ru^{III}Ru^{II}/Ru^{III}Ru^{II}Ru^{II}$ to $Ru^{III}Ru^{II}Ru^{II}/Ru^{III}Ru^{II}Ru^{II}$ (see Section 2.13).



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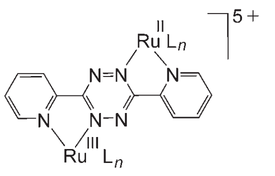
2.3. *Beyond "Spacers": Structurally Sophisticated Bridging Ligands*

Conventional molecular bridges contain donor atoms for metal binding in a bis-monodentate (**1**),[10–12] bis-bidentate (**11**),[53–55] bis-tridentate (**12**),[56–59] or bis-tetradentate[60] fashion (**13**), connected to a "spacer" which typically ensures π conjugation and determines the metal–metal distance.

Within the ligand design concepts of supramolecular chemistry other, more sophisticated bridge architectures may be employed in mixed-valence chemistry. Additional aspects include stereochemistry, such as conformational or configurational isomerism,[61] and added physical properties and reactivity, for example, luminescence or proton transfer.[62]

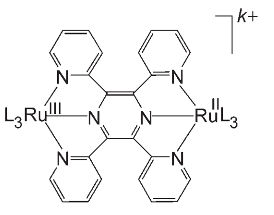
Even complexes with two equivalent and approximately octahedrally coordinate metal centers can thus exist as *meso*



L = NH_3 , $n = 4$

L = bpy, $n = 2$

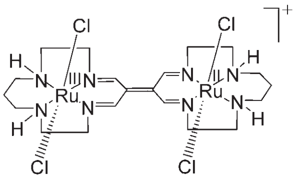
11



$L_3 = 3NH_3$ or

$L_3 = Cl^- +$ bidentate ligand

12



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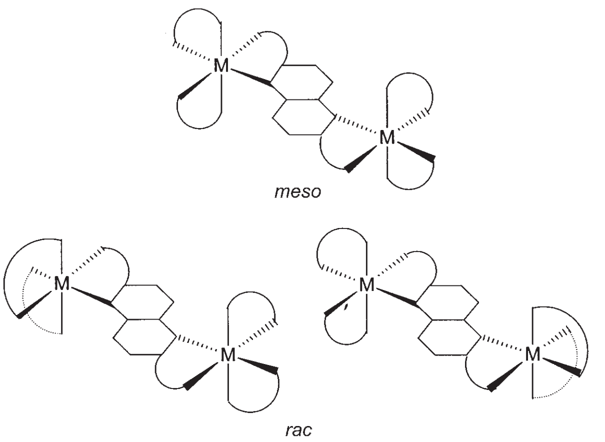
(ΔΛ) and *rac* (ΛΛ/ΔΔ) stereoisomers in a situation as depicted in Scheme 2.[61,63,64] The corresponding mixed-valent states in general showed little difference in their



Scheme 2.

electrochemical and spectroscopic features,[61] suggesting that the coordination framework is largely unaffected and that the valence-exchange mechanism is essentially unperturbed by this kind of isomerism. Similar results were reported for complexes with tris-bidentate ligands, such as HAT (e.g. complex **6**).[65]

We have recently reported[66] a system $[(acac)_2Ru(\mu\text{-}abpy)Ru(acac)_2]$ in which the molecular framework structures (twisting) of the *meso*/*rac* isomers are significantly different. The result can be best described as a radical-bridged mixed-valent arrangement $[Ru^{III}(abpy^{\bullet -})Ru^{II}]$ (see Figure 7 in Section 2.5). Again, the absorption-spectroscopy data differ only slightly, however, the most sensitive parameter, the g factor anisotropy from EPR spectroscopy, differs clearly for the reduced and oxidized forms.[66b]

Proton-transfer reactions of bridging[62] or ancillary[56b] ligands can affect valence exchange. In general, the increased donor strength of deprotonated ligands stabilizes higher oxidation states and mixed-valent intermediates in hole-transfer situations (Figure 3) by raising the energy of the high-lying occupied molecular orbitals (MOs). Such effects were described, for example, for mixed-valent complexes **14** with bis(benzimidazolate) bischelate ligands[62a] or other bridges containing heterocycles,[62b–e] and for the first dithiolate-bridged diruthenium(III,II) compound **15** (trpy = 2,2′:6′,2″-terpyridine).[62f] In **15**, the two one-electron oxidation processes which produce an intermediate (with $K_c = 10^{3.7}$ and $\lambda_{max}(\text{IVCT}) = 1822$ nm, $\varepsilon = 4000\,\text{M}^{-1}\,\text{cm}^{-1}$) collapse into one two-electron process on protonation of an N atom in the bridge.[62f] This response of mixed-valent systems towards pH value has been referred to as “switching behavior of redox communication” (see Section 2.12 and Figure 10).[62]

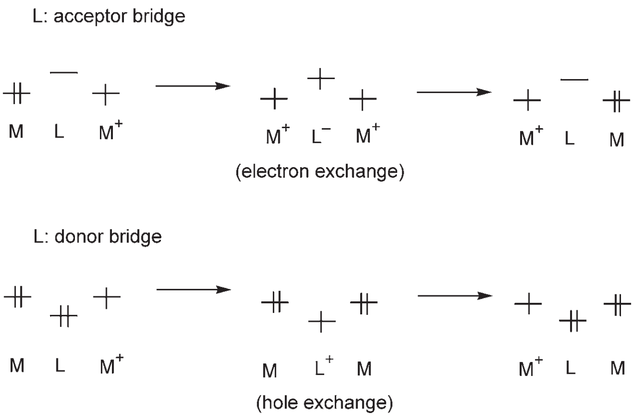
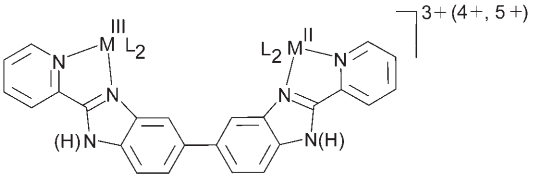


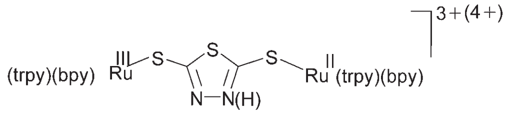
Figure 3. Two mechanistic alternatives of L-mediated valence exchange between M and M^+, involving low-lying unoccupied (top) or high-lying occupied orbitals (bottom).



M = Ru, Os

L = bpy, phen

14



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2.4. Enhanced Metal–Metal Interaction through Frontier-Orbital Tuning

Valence exchange in mixed-valent complexes can be described involving either electron transfer through a low-lying unoccupied orbital of an acceptor bridge or hole transfer through a high-lying occupied orbital of a donor bridge (Figure 3).[67–69] The alternatives can be distinguished by the spin distribution or metal-exchange effects:[67] Replacing ruthenium(II) by the stronger[70] π-donating osmium(II) results in an increased stability constant (comproportionation constant) K_c of the mixed-valent intermediate in an electron-transfer situation whereas the opposite holds for the hole-transfer alternative (Ru^{III} is a better π acceptor than Os^{III}). In agreement with basic MO theory for a three-center arrangement, the spin distribution in M−(μ-L)−M differs considerably, involving no apparent contribution from the central bridge for electron-transfer (three-electron count) but significant bridge effects for hole-transfer (five-electron situation; Figure 4).[54b,64b]

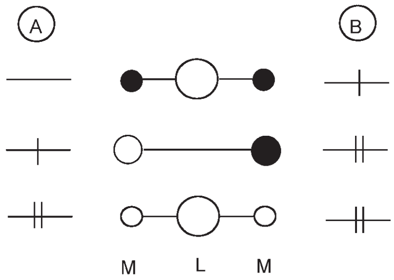
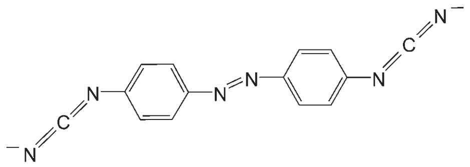


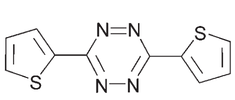
Figure 4. Orbital characteristics for an M-L-M three-center arrangement and different spin distribution for the three-electron (A) and five-electron counts (B). Only (B) implies significant spin density on the bridge L.

The situation that both hole- and electron-transfer exchange mechanisms can operate simultaneously, and to a similar extent, is particularly attractive because it may lead to enhanced metal–metal interaction; such a case has been proposed for $[(\mu\text{-adpc})\{Ru(bpy)(trpy)\}_2]^{3+}$ ($adpc^{2-}$ = 4,4′-azodi(phenycyanamido)) in which the ruthenium atoms are

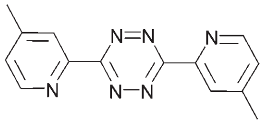


adpc^{2-}

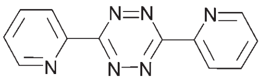
separated by about 19.5 Å and there is a large comproportionation constant of $K_c = 10^{13.1}$.[69] A long-wavelength absorption at 1920 nm ($\varepsilon = 10\,000\,M^{-1}\,cm^{-1}$) was observed for the intermediate which differs considerably from the absorption of $adpc^{\bullet-}$; however, the reasonable alternative of a ligand-centered (radical) species has yet to be ruled out by more specific identification methods such as EPR spectroscopy (see Section 2.5).



bttz



bmptz



bptz

3,6-Bis(2-thienyl)-1,2,4,5-tetrazine (bttz),[71] a member of the remarkable family of tetrazine-based bridging ligands,[72] has been studied recently to evaluate its bridging-ligand characteristics. 1,2,4,5-Tetrazines are distinguished by a very low-lying π* MO centered on the four nitrogen atoms. Using the less common bttz[73] ligand it was observed that the dinuclear bis(2,2′-bipyridine)ruthenium complex forms an unusually stable mixed-valent intermediate $[(\mu\text{-bttz})\{Ru(bpy)_2\}_2]^{5+}$ with $K_c = 10^{16.6}$ and an intervalence charge-transfer (IVCT) absorption at the atypically high energy of 11100 cm^{-1} (990 nm; $\varepsilon = 1650\,M^{-1}\,cm^{-1}$).[71] Surprisingly, the diosmium(III,II) analogue $[(\mu\text{-bttz})\{Os(bpy)_2\}_2]^{5+}$ did not exhibit an enhanced K_c value.[71]

Thiophene containing molecules have found wide interest and application in materials chemistry,[74,75] including mixed donor–acceptor containing polythiophene systems with decreased band gaps.[76]

The most striking result is the unexpectedly strong stabilization of the $Ru_2^{III,II}$ state of the bttz containing complex ($K_c = 10^{16.6}$) in comparison to related complexes containing, for example, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz; $K_c = 10^{8.5}$;[71] bpy as ancillary ligands in all cases). The destabilization of the Ru_2^{II} state and the much higher K_c value also led to the isolation of the mixed-valent state as $[(bpy)_2Ru^{III}(\mu\text{-bttz})Ru^{II}Ru(bpy)_2](PF_6)_5$.[71] In contrast, the diosmium analogues exhibit a reversed pattern of electrochemical stability. The K_c value of the diosmium bmptz complex is higher than that of the diruthenium species ($K_c = 10^{11.4}$ and $10^{9.0}$, respectively). This result is in agreement with those obtained for other π-acceptor bridged $M_2^{III,II}$ complexes (M = Ru or Os).[67] However, at $10^{7.8}$, the K_c value of the diosmium complex of bttz is much smaller than the exceptional value of $10^{16.6}$ of the diruthenium species of the same ligand, reflecting a dominating π-donor contribution attributed to the thienyl rings. This unexpected situation is further illustrated by the result that the K_c of the diosmium complexes is smaller in the case of bttz than bptz or bmptz containing complexes, whereas K_c is much larger in the diruthenium complex of bttz than those of bptz or bmptz.

The unexpected reverse effects of the bttz complex may be rationalized by the three-center model and the concepts of electron and hole transfer (Figure 3, Figure 4), considering the established π-donor capability of thiophene.[75,76]

Bptz and bmptz are mainly π-accepting ligands and the valence-exchange interaction between the two metal centers takes place by the electron-transfer mechanism (Figure 3) involving the empty π* orbital of bptz or bmptz. Since bttz has two π-donating thienyl substituents in addition to the π-accepting tetrazine ring, the metal centers bridged by bttz should be able to interact by both the electron- and the hole-transfer mechanisms. Interaction of the electron-accepting trivalent ions with the mediating HOMO involving the thienyl donor will reduce the electron density available for binding the second, divalent metal center. Ruthenium(III) is a far better π-acceptor than osmium(III), and hence ruthenium can take advantage of both the electron- and hole-transfer pathways with bttz, whereas osmium can interact only by the electron-transfer route (Figure 5). Apparently, this situation leads to a doubling of ΔE and thus to an exceptionally high K_c value for $[(\mu\text{-bttz})\{Ru(bpy)_2\}_2]^{5+}$.

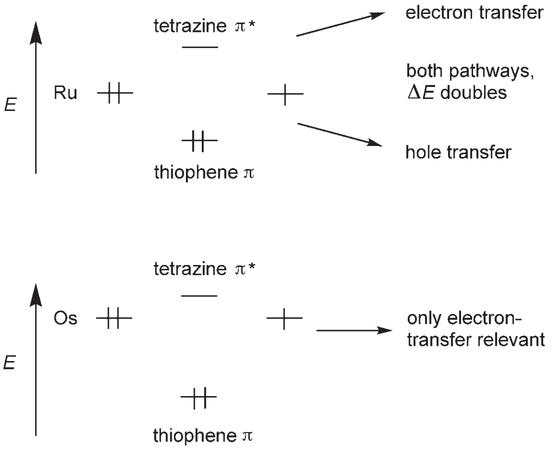
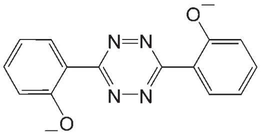


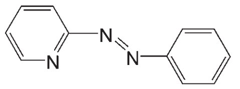
Figure 5. Orbital interaction diagrams for possible simultaneous hole- and electron-transfer pathways for valence exchange in the case of $\{(\mu\text{-bttz})[M(bpy)_2]_2\}^{5+}$ ions (bttz = 3,6-bis(2-thienyl)-1,2,4,5,-tetrazine). The scheme shows the operation of both electron- and hole-transfer mechanisms for M = Ru (top) but only the electron-transfer mechanism for M = Os (bottom).[71]

The strong metal–metal coupling in $[(bpy)_2Ru^{II}(\mu\text{-bttz})Ru^{III}(bpy)_2]^{5+}$ is also evident from the EPR spectrum of this compound at low temperatures ($g_1 = 2.479$, $g_2 = 2.313$, $g_3 = 1.807$).[71] The high g factor anisotropy $g_1 - g_3 = 0.672$ and the deviation of the calculated isotropic g value (2.218) from the free electron g factor ($g_e = 2.0023$) points to predominantly metal-centered spin corresponding to a Ru^{III} center. The osmium analogue of this compound as well as the bptz- or bmptz-bridged mixed-valent complexes of ruthenium and osmium are EPR silent even at 4 K. This situation is attributed to rapid relaxation involving close-lying excited states because of weaker metal–metal coupling and, in the case of osmium systems, because of the high spin-orbit coupling of the metal.

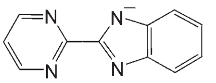


donor / acceptor / donor

$boptz^{2-}$



pap



acceptor / donor

$bimpm^-$

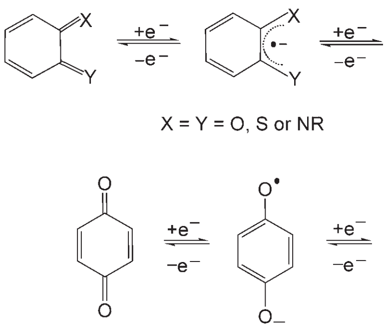
In addition to the mixed donor–acceptor–donor bridging ligands $adpc^{2-}$ and bttz, the similarly constructed 3,6-bis(2-oxidophenyl)-1,2,4,5-tetrazine ($boptz^{2-}$) system reported very recently has been employed for diruthenium complexes.[77a] In this case, the result is a remarkable sensitivity of the system towards peripheral coordination by ancillary ligands (Figure 6; see also Section 2.6). For the intermediate $[L_2Ru(boptz)RuL_2]^n$, the donating $L = acac^-$ ($n = 1-$) stabilizes the higher oxidation state +III of both ruthenium centers to give a radical complex, whereas the weak acceptor L = bpy allows Ru^{II} to be formed and thus a mixed-valent situation ($n = 3+$).[77a] With the strong π-acceptor L = pap the first oxidation appears to occur on the phenolate part of the bridge to yield a phenoxyl complex[78] intermediate. Synergistically interacting pyrimidine acceptors and benzimidazolate donors were also invoked for the stabilization of mixed-valent states $[(\mu\text{-bimpm})\{M(bpy)_2\}_2]^{4+}$ (M = Ru, Os).[77b]

2.5. Mixed Valence with Non-Innocent Bridging Ligands?

Non-innocent, that is, redox-active bridging ligands, can occur in the form of strongly reducible acceptors such as *o*- and *p*-quinones[64b,79,80] or azo compounds[81] or, conversely, as easily oxidizable donors, such as catecholates (Scheme 3) or hydrazides. In such cases, the alternative of localized [Eq. (4), **A**] versus delocalized [Eq. (4), **B**], mixed-valent description may be complemented by a third scenario [Eq. (4), **C**] which does not have metal-centered mixed valence but an organic radical bridge.

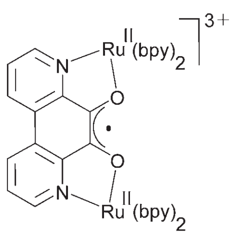
$[(acac)_2Ru^{III}(\mu\text{-boptz}^{\bullet 3-})Ru^{III}(acac)_2]^-$	$[(bpy)_2Ru^{II}(\mu\text{-boptz}^{2-})Ru^{III}(bpy)_2]^{3+}$	$[(pap)_2Ru^{II}(\mu\text{-boptz}^{\bullet -})Ru^{II}(pap)_2]^{3+}$
K_c: $10^{12.0}$	K_c: $10^{6.0}$	K_c: $10^{2.4}$
NIR: no NIR band	NIR: IVCT absorption around and beyond 2000 nm	UV/Vis-NIR: no NIR band, phenoxyl radical band at 488 nm
EPR: $g_{av} = 2.073$, $\Delta g = g_1 - g_3 = 0.48$	EPR: Isomer 1: $g_{av} = 2.180$, $\Delta g = 0.67$ Isomer 2: $g_{av} = 2.130$, $\Delta g = 0.45$	EPR: $g_{iso} = 2.0046$
antiferromagnetically coupled isovalent three-spin system, spin on Ru	mixed-valent intermediate, spin on Ru	radical complex spin on ligand

Figure 6. Effect of ancillary ligands on the metal–ligand valence-state distribution in ($boptz^{2-}$)-bridged diruthenium complexes.[77a]



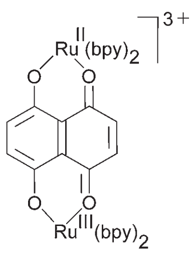
Scheme 3.

To assess this oxidation-state ambiguity, a number of techniques are available, however, great care should be taken in drawing conclusions from limited information. For example, the two-step electron transfer occurring on a non-innocent ligand is electrochemically indistinguishable from the two-step metal-based electron transfer involving a mixed-valent intermediate. Furthermore, owing to low-lying intraligand or charge-transfer transitions many radical complexes[82] will exhibit absorption features of variable intensity in the near-infrared (NIR) region, and such absorptions can easily be mistaken for intervalence charge transfer bands.[83,84] Frequently, the observation of an intermediate with a near-infrared band has been taken as sufficient and convincing evidence for a mixed-valent situation although a highly non-innocent, for example, quinone-type bridging ligand was present.[68b,69,85] Only in a few instances were such intermediates clearly identified as either semiquinone (**16**)[64b] or mixed-valent species (**17**).[80a]



$g = 2.05, 2.03, 1.98$

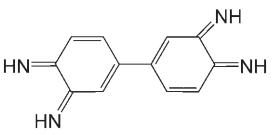
16



$g = 2.33, 2.01, 1.88$

17

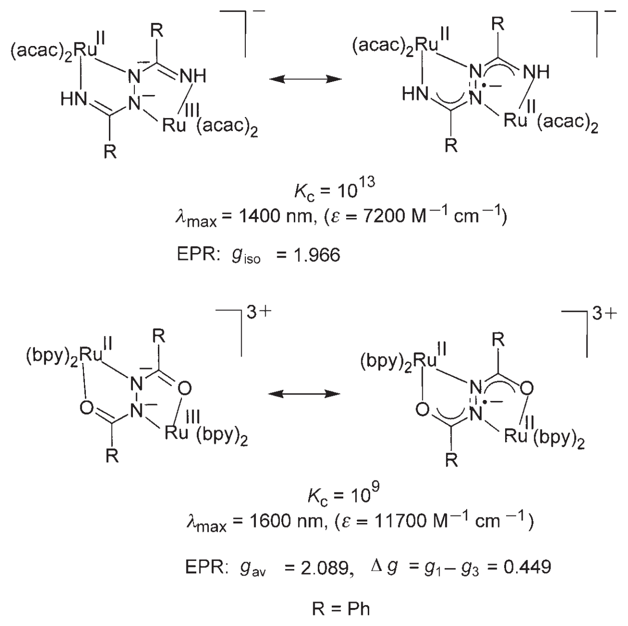
With reduced 3,3′,4,4′-tetraimino-3,3′-4,4′-tetrahydrobiphenyl (L) the anionic bis(bis-acetylacetonatoruthenium) complex is a radical species $\{Ru^{II}(L^{\bullet-})Ru^{II}\}$ whereas the cation is a $\{Ru^{III}(L)Ru^{II}\}\leftrightarrow\{Ru^{IV}(L^{2-})Ru^{III}\}$ mixed-valent complex.[80b] Both intermediates exhibit near-infrared absorption bands, however, EPR spectroscopy showed a clear difference, $g = 2.003$ for the anion and $g_{\perp} = 2.197$, $g_{\parallel} = 1.922$ for the cation.[80b]



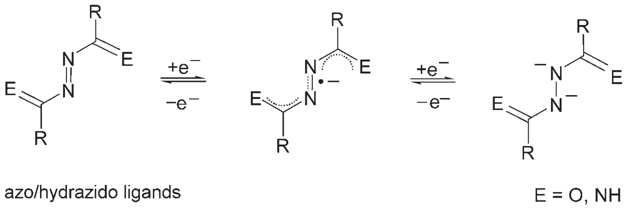
L

In fact, the most compelling evidence for the presence (or absence) of a mixed-valent situation usually comes from EPR spectroscopy because the involvement of the metal center(s) in the singly occupied molecular orbital (SOMO) manifests itself through large *g* factor anisotropy (high spin-orbit coupling constants of Ru and Os)[86] and rapid relaxation (resulting in broad lines so that the EPR signal can only be detected at low temperatures).[67] Radical complexes, on the other hand, typically exhibit narrow EPR lines, better resolved spectra, signal intensity at room temperature, and a relatively small degree of *g* factor anisotropy.[82]

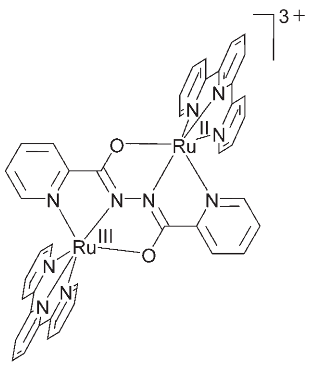
Between the extremes of predominantly metal- or ligand-centered valence (and spin) lies a region of fractional metal/ligand electron delocalization, which has been supported by recent theoretical studies[87a] on mononuclear *o*-iminoquinone complexes of $\{Ru(acac)_2\}$.[87b] A revealing case in point for dinuclear complexes are the compounds of azo/hydrazido ligands (Scheme 4) of which the series with E = O exhibits a continuum ranging essentially from $Ru^{III}Ru^{II}$ mixed-valent cases [Eq. (4), **A**,**B**] to a near radical situation [Eq. (4), **C**]; the spin distribution between ligands and metals is influenced not only by the acceptor/donor substitution pattern of the groups



Scheme 4.



R[54b] but also by the possibility to introduce another coordination function R, such as 2-pyridyl in complex **18** with a bis-tridentate bridge.[59] In this case, the more extended conjugation of the π system leads to a greater radical character and thus to a diminished mixed-valent nature of the intermediate $[L_nRu(\mu\text{-BL})RuL_n]^{3+}$ (Table 2).



18

Table 2: EPR Data of paramagnetic intermediates.

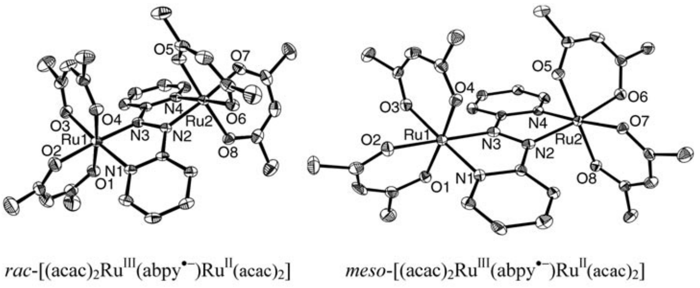
Parameter	**18**[59]	$[\{(bpy)_2Ru\}_2(\mu\text{-adc-Ph})]^{3+}$ [54b][a]
g_1	2.150	2.344
g_2	2.120	2.003
g_3	1.953	1.895
g_{av}[b]	2.076	2.089
g_1-g_3	0.197	0.449
	radical/mixed-valent	mixed-valent

[a] See Scheme 4, R = Ph, E = O. [b] $g_{av} = [(g_1^2+g_2^2+g_3^2)/3]^{1/2}$.

The related new compounds from Scheme 4 (E = NH) are predominantly diruthenium(II)-radical species with correspondingly narrow EPR lines[84] although all the intermediates $[(\mu\text{-dih-R})\{Ru(acac)_2\}_2]^-$ (dih-R = substituted 1,2-diiminohydrazido ligands), have distinct absorption bands in the near-infrared region around 1400 nm. The NIR absorption of an intermediate from a two-step electron-transfer series should thus never be taken alone as sufficient evidence for mixed valence.

Remarkably, however, it is possible to combine the radical-intermediate state of a non-innocent bridging ligand with a diruthenium(III,II) mixed-valent situation. Using the abpy ligand again (see Section 2.1), this time as a structurally established anion radical $abpy^{\bullet-}$ with a typical separation of the central nitrogen atoms of $d_{NN} \approx 1.37$ Å in differently twisted stereoisomeric complexes (Figure 7),[66] the resulting neutral species $[(acac)_2Ru(\mu\text{-abpy})Ru(acac)_2]$ is best formulated as a $\{Ru^{2.5}(abpy^{\bullet-})Ru^{2.5}\}$ mixed-valent system according to experimental results and DFT calculations.[66] Such configurations have been discussed as low-lying metal-to-ligand charge transfer (MLCT) excited states [Eq. (9)] of homovalent species.[87,88]

$$\{Ru^{II}(\mu\text{-BL})Ru^{II}\} \rightarrow {}^*\{Ru^{III}(\mu\text{-BL}^{\bullet-})Ru^{II}\} \qquad (9)$$



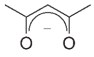
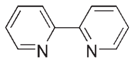
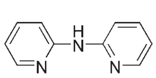
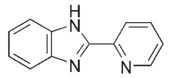
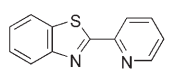
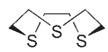
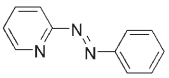
	rac-$[(acac)_2Ru^{III}(abpy^{\bullet-})Ru^{II}(acac)_2]$	$meso$-$[(acac)_2Ru^{III}(abpy^{\bullet-})Ru^{II}(acac)_2]$	
d_{NN} [Å]	1.372(4)	1.374(11),	1.352(17)
ω [°]	26.1	15.5,	0.0
K_c	$10^{18.3}$	$10^{18.3}$	
λ_{max} [nm] (ε [M^{-1} cm^{-1}])	835 (29000)	848 (29000)	

Figure 7. Characteristics of isomeric mixed-valent complexes with a radical bridge (two crystallographically independent molecules for the *meso* isomer).[66]

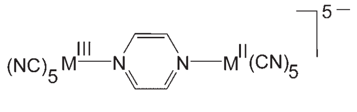
2.6. Influence from the Periphery: Non-Standard Ancillary Ligands

The common ancillary ("spectator") ligands in ruthenium mixed-valence chemistry have been the electronically rather innocent ammine, halide, or pyridine-type ligands (Table 3).[10–12] Such co-ligands are not expected to influence the metal oxidation state or the metal–bridge interaction to a significant extent. However, it was early recognized[89] that even a moderately π-accepting ancillary ligand, such as 2,2′-bipyridine can decrease an acceptor bridge-mediated metal–metal interaction (Figure 3, top) by competing with that bridge for the π back donation, that is, for π electron density

Table 3: Some ancillary ligands used in mixed-valent diruthenium chemistry.

Type	Ligand
π-donors	 acac⁻ Cl^-
innocent	NH_3
weak π-acceptors	 bpy  dpa  2-(2-pyridyl)benzimidazole  2-(2-pyridyl)benzothiazole  [9]aneS$_3$
strong π-acceptors	 pap CN^-

from ruthenium(II) centers. Competition can similarly occur from peripheral cyanide ligands (**19**, M = Ru) which diminish the metal–metal interaction in an electron-transfer situation[90] or from strongly π-accepting and thus Ru^{II}-stabilizing pap co-ligands which may even effect a change in oxidation-state distribution within complexes (Figure 6).[77]



M = Ru, Os

19

On the other hand, σ- and π-donating co-ligands, such as $acac^-$ stabilize higher oxidation states, such as Ru^{III} or Ru^{IV}, and thus can effect yet a another different oxidation-state situation (Figure 6).[77] Table 3 gives a list of some typical kinds of ancillary ligands, Table 4 demonstrates the effect of different ancillary ligands on the K_c value for a particular situation, that is, for intermediates with the $\{Ru^{2.5}(\mu\text{-bptz})Ru^{2.5}\}$ configuration.

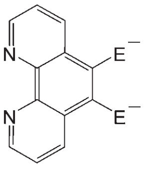
Table 4: Effect of ancillary ligands on the comproportionation constants (K_c) of $[(L_xRu)_2(\mu\text{-bptz})]^{n+}$.

L_x	n	$Ru^{III}Ru^{II}/Ru^{II}Ru^{II}$ couple; $E_1°$ [V][a]	$Ru^{III}Ru^{III}/Ru^{III}Ru^{II}$ couple; $E_2°$ [V][a]	K_c	Ref.
$([9]aneS_3)(Cl)$	3	1.36	1.84	$10^{8.0}$	[104]
$(bpy)_2$	5	1.52	2.02	$10^{8.5}$	[64a]
$(acac)_2$	1	0.17	0.97	$10^{13.6}$	[99]
$(NH_3)_4$	5	0.69	1.58	$10^{15.0}$	[55]

[a] Potentials versus saturated calomel electrode (SCE). Measurement details can be found in the corresponding references.

2.7. The Role of the Donor Atoms at the Metal–Ligand Interface

The most frequently used donor atom in ruthenium mixed-valence chemistry has been nitrogen because of the typically inert Ru–N bonds in various oxidation states[4] and because of the many variations possible. Replacement of NR or NH in the bridge by the more electronegative and less basic oxygen facilitates ligand reduction which can even result in different oxidation-state combinations as has been shown for 5,6-disubstituted 1,10-phenanthrolines.[91] The unsymmetrically bridging bischelate ligands Q^{n-} form redox series $[(\mu\text{-}Q)\{Ru(acac)_2\}_2]^k$ of which the $k = 1-$ form exhibits striking differences from the other members (Figure 8): For E = O the EPR signal shows metal-based spin and a near-IR band, compatible with a $\{Ru^{III}(Q^{2-})Ru^{II}\}$ mixed-valent description. On the other hand, with E = NH the EPR result indicates ligand-centered spin which supports a $\{Ru^{II}(Q^{\bullet-})Ru^{II}\}$ formulation. Apparently, the change from more electronegative O to more basic NH favors the Ru^{II} oxidation state enough to shift the electronic structure away from the mixed-valent configuration (and towards the homovalent situation).[91]



E = O, NH

Q^{2-}

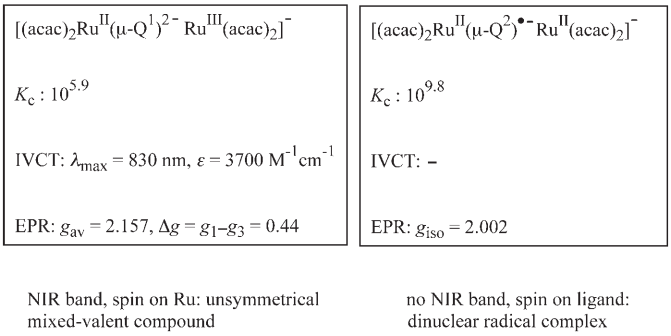
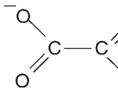


Figure 8. Variable valence distribution in diruthenium complexes bridged by Q^n (E = O (left) or NH (right), see Section 2.7).[91]

Mixed O,N-donor bridging ligands are not uncommon both for mixed-valent and radical dinuclear complexes.[54,59,84,92] Of course, there are also established all-oxygen coordinated diruthenium mixed-valent complexes with exclusively oxygen-donor-containing bridges,[80a] a straightforward example being $[(acac)_2Ru(\mu\text{-ox})Ru(acac)_2]^x$ (ox^{2-} = oxalato) with $K_c = 10^{5.0}$, $\lambda_{max}(IVCT) = 1430$ nm ($\varepsilon = 500\,M^{-1}cm^{-1}$) and considerable g factor anisotropy of the EPR signal.[93] Broadening of the $\nu_{as}(CO)$ band in the infrared spectrum only for the mixed-valent intermediate[93] suggests valence exchange on the vibrational time scale (see Section 2.13).[30]



ox^{2-}

The potential for S-donor atoms in the bridge remains largely unexplored in diruthenium mixed-valence chemistry (see compounds **8** and **15** and Figure 5).[44b,62f,71,94]

2.8. The Heavy-Metal Effect: Ruthenium versus Osmium

The fact that the diosmium analogue of the Creutz–Taube ion was reported 19 years later[70a] than the ruthenium original[6] indicates that the chemistry of this heavier homologue can be quite different. Apart from the much more inert bonds to the ligands (a disadvantage for synthesis but an advantage in terms of robustness), the osmium atoms are distinguished by an altered oxidation-state preference, that is, Os^{III} is preferred over the strongly π-donating[70] Os^{II}; the physical properties are often affected by the much higher spin-orbit coupling constant of that 5d element.[86] For the mixed-valent complexes these different atomic properties translate into:

- The K_c values tend to be higher for acceptor-bridged systems[70a,83] but lower for donor-bridged compounds.[62a,67] The reason lies in the stronger π-donor capability of osmium(II) compared to ruthenium(II), which is effective in an electron-transfer valence-exchange situation (Figure 3, top) whereas the hole-transfer alternative

(Figure 3, bottom) profits from the stronger π-acceptor character of ruthenium(III) over osmium(III).[67]

- Osmium complexes are distinguished by more complex optical spectra[14,70a,83,94] owing to the spin-orbit enhanced intensities of normally "forbidden" transitions (e.g. triplet or quartet absorptions). Even simple systems, such as the diosmium analogue[70a] of the Creutz–Taube ion **1** or the decacyano diosmium compound **19**, M = Os, exhibit numerous detectable bands in the NIR and IR regions[94] which originate from several spin-orbit allowed intervalence charge transfer transitions.
- The large spin-orbit coupling of Os^{III} (3000 cm^{-1}) versus Ru^{III} (1200 cm^{-1}) or even Fe^{III} (ca. 500 cm^{-1})[86] leads to increased *g* factor anisotropy in the EPR spectra,[83] as evident, for example, for the complexes $[M(CN)_5(NO)]^{3-}$.[95] Associated is an increase in linewidths, even to the point of "EPR silence".[67,83,96]

Table 5: Electrochemical and intervalence-absorption characteristics of diruthenium (III,II) complexes.

Formula	K_c[a]	λ_{max} [nm] (ε [M^{-1} cm^{-1}])	Ref.
$[(pap)_2(Cl)Ru(\mu\text{-tppz})Ru(Cl)(pap)_2]^{3+}$ (**12**)[b]	$10^{3.9}$	1890 (3800)	[56b]
$[(NH_3)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (**1**)	$10^{6.6}$	1570 (5000)	[6]
$[(acac)_2Ru(\mu\text{-bptz})Ru(acac)_2]^{+}$ (**11**)	$10^{13.6}$	1238 (20)	[99]
$[(NH_3)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{5+}$ (**11**)	$10^{15.0}$	1450 (500)	[55]

[a] Measurement details can be found in the corresponding references. [b] tppz = Tetrakis(2-pyridyl)pyrazine.

For instance, paramagnetic complexes [(μ-BL){Os(bpy)$_2$}$_2$]$^{5+}$, (BL = bptz,[96] bmptz,[71] abpy,[83]) have variable, potentially rather large *g* factor anisotropies $g_1 - g_3 = 0.007$–0.25 yet they still must be described as radical complexes of diosmium(II) species. The diosmium(III,II) compounds [(μ-adc-R){Os(bpy)$_2$}$_2$]$^{3+}$ (adc-R = azodicarbonyl ligands, see Scheme 4), on the other hand, are EPR silent even at 4 K,[67,96] in spite of an S = $^1/_2$ ground state. Temperature-dependent magnetism of complexes [(μ-adc-R){M(bpy)$_2$}$_2$]$^{3+}$ (M = Ru or Os,[54b,96]) or of other multinuclear ruthenium compounds[97] show spin-orbit-coupling-enhanced spin admixture of S = $^1/_2$ and S = $^3/_2$ states which requires further investigation.

2.9. Independence of Electrochemical and Spectroscopic "Coupling" Effects

For compounds like the Creutz–Taube ion, that have a homogeneous kind of coordination[10–12] with bis-monodentate acceptor bridges, there has long been the assumption that the electrochemically determined comproportionation constant K_c reflects the metal–metal interaction in a similar fashion and to a similar extent as the electronic interaction energy, which is derived from the energy and intensity of the IVCT band according to Equation (7).[27] However, the use of increasingly variegated bridging ligands, especially with chelate functions of variable denticity (bis-bidentate, bis-tridentate, or bis-tetradentate ligands)[55–60] has shown that these two manifestations of metal–metal interaction may not run in parallel but can be very different in magnitude.[98] In comparison to the Creutz–Taube ion as a standard, Table 5 illustrates cases with small K_c values and intense IVCT bands (bis-tridentate acceptor bridges)[56–58] as well as examples with very large K_c values but weak or non-observable IVCT features, typically exhibited by diruthenium(III,II) compounds with tris- or bis-bidentate acceptor bridges.[45a,46,55,99]

Clearly, both situations refer to different "coupling" mechanisms: on the one hand, there is the Coulombic/charge dominated K_c value [Eq. (3)] and on the other, the orbital overlap-controlled interaction energy which can be estimated from the charge-transfer-band energies and intensities using [Eq. (7)].[17,19] As a caveat, drawing quick conclusions about "weak" or "strong" coupling based on only one kind of physical measurement should be avoided.

2.10. Beyond Distance Dependence

The distance dependence of the metal–metal interaction in mixed-valent diruthenium complexes has been investigated several times for series of closely related systems, that is, having identical "end groups" but different lengths of the (conjugated) "spacer"[15,21,57b,100] made up from aromatic rings, $(CH)_n$ or C_n entities. The quantitative analysis of such series gives parameters such as "decay factors". While it has been clear that distance alone cannot be the only factor influencing the metal–metal interaction (for example, the interaction is greatly diminished non-conjugated systems)[10] the role of the metal/ligand interface[101] involving the orbital overlap between π type MOs of the ligand "end group" and of the metal dπ orbitals needs to be considered (Figure 9). Amongst the more striking examples are the pairs of complexes [(μ-BL){ML$_n$}$_2$]^k, (BL = bpym vs. bptz), for which the metal–metal interaction is generally weaker for the 2,2′-bipyrimidine (bpym) compound in spite of the smaller metal–metal distance (5.5 Å vs. 7.8 Å for complexes of bptz).[53b,55,64a,102]

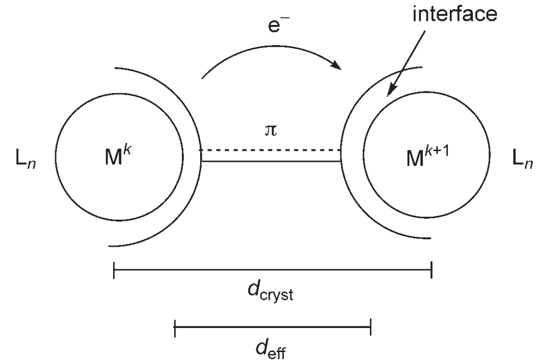


Figure 9. Interfaces between metal and bridging ligand in mixed valence complexes. d_{cryst} = crystallographically determined separation, d_{eff} = distance between "effective electron-transfer sites".

An equivalent approach is to redefine the distance as used in Equation (7) and not use the crystallographic metal–metal distance d_{cryst} but a smaller value d_{eff}, the distance between "effective electron-transfer sites", the shortening being associated with the delocalization in the bonding between the ligand end group and the metal center.[15,20]

2.11. Vision of a Classless World of Mixed Valence

A dated (1967)[2] but still popular classification scheme put forward by Robin and Day for mixed-valent systems, including molecules, metal complexes, and solid-state materials, defines three situations for valence exchange:

- The singular case "Class I" implies essentially zero metal–metal interaction, for example, owing to very different metal environments (see for instance the mono-chloro complex intermediate in Scheme 1) or large spatial separation (isolation).
- The other extreme, also a singular situation, is called "Class III" and implies activationless electron transfer between equivalent metal sites, thus constituting an electron delocalized system with averaged valency and possibly fractional oxidation states. These mixed-valent compounds are of great interest because of their new properties resulting from a new electronic situation, however, the absence of an activation barrier leaves no opportunity for dynamic effects.
- Only Class II is of interest from a dynamics point of view, because a small but non-zero barrier for valence exchange may exist and the typical manifestations of mixed valence (Section 1.2) should be present. Class II behavior is particularly interesting for apparently symmetrical systems with formally equivalent electron-transfer sites where the typical sensitivity of such mixed-valent arrangements towards the medium (solvent, counter ions)[14,26,103] becomes clear.
- The different and sometime contradictory manifestations of mixed-valence for ruthenium and osmium complexes[14] have prompted Meyer and co-workers to define a new "Class II–III" or "borderline" situation in which the rate of intramolecular electron transfer is on the order of the relaxation time (10^{-12}–10^{-13} s) of the solvent. With small electron-transfer barriers, the role of the environment becomes more pronounced.[103] The Creutz–Taube ion itself may be considered such a borderline case which would help to explain the extended discussion around its proper classification.[10–18]

It may be argued that the sometimes bewildering I, II, II–III, III classification schemes may be abolished in due course despite their historical significance during the development of the field. Instead, the proper characteristics of the mixed-valent compounds should be used to define the symmetry and the barrier for valence exchange for each experimental method considering the appropriate time frames.[30]

2.12. Wiring, Switching, and Molecular Computing: Mixed-Valence Concepts for Molecular Electronics

The original purpose for trying to obtain mixed-valent complexes like the Creutz–Taube ion was the possibility to study intramolecular electron transfer between equivalent metal sites in a stable, well-defined coordination compound.[4] Later aspects involved the test-system character of such species for electron-transfer theory[10,14,17–19] and for spectroscopic techniques.[20] Given that electron transfer between organized functional atoms or molecules is an essential process within the rapidly growing field of molecular electronics[15,16,22–24] there have been proposals to use mixed-valent systems for controlled charge propagation ("molecular wires")[15,16,21,22a,b] and for information processing ("molecular switching") within molecular devices.[16,22a,c] Examples for wires include complexes with extended bridging ligands involving (arylene)$_n$, (CH)$_n$, or C$_n$ components,[15,16,21,22a,c,57b,100] and for switching (Figure 10)[16,22c] molecules such as **14** or **15** (Section 2.3).[62]

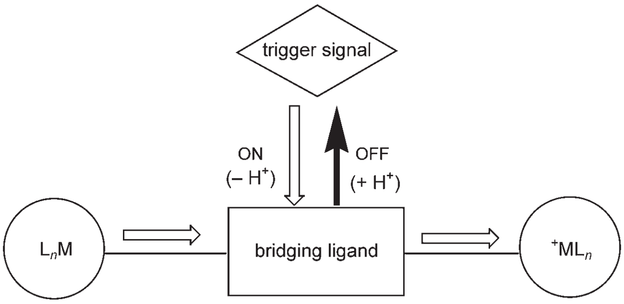


Figure 10. Response of mixed-valent systems, in this case to the change in pH value (switching effect in redox communication).

Whereas the electron or hole conduction of linear or nonlinear molecular wires is connected to the familiar concept of conjugation, including, for example, metalla-π-systems, the switching function requires the existence of two stable states with different physical properties ("bistability"), reversibly interconvertible through controlled external triggering or stimulation. Such triggering may involve irradiation or concentration (e.g. pH value) changes (Figure 10),[62] and the response may be light emission or charge movement, and subsequent structural, spectroscopic, or other reaction, which may eventually allow the construction of molecular logical devices.[16,22]

More recently, the concept of "molecular computing" has been put forward[24b] with binary information being encoded in the molecular configuration (Figure 11); quantum-dot cellular automata (QCAs)[24b] were proposed based on smaller[23] or larger mixed-valent systems.[24]

Although not all the proposed systems[24a] may be chemically feasible, for example, because of intramolecular electron transfer (see Section 2.2.2),[49,51] the potential for bistability in a valence-localized situation would allow for possible information creation (and propagation, if used in an extended system) and for the development of logical functions.[24]

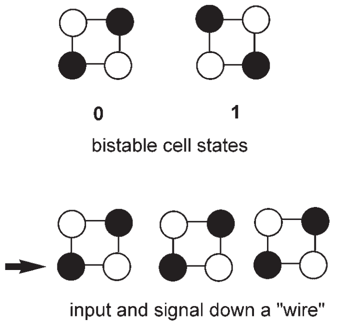
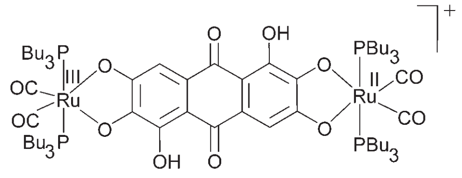


Figure 11. The concept of "molecular computing" with mixed valent tetranuclear systems;[24b] ○ and ● indicate different oxidation states.

2.13. Access to Ultrafast Electron-Transfer Dynamics through the Synthesis of Complexes

The crucial role of spectroscopic time scales for the investigation of valence (de)localization in mixed-valent compounds has already been pointed out.[30] In a favorable case, such as **20**, it may be possible to detect fully delocalized spin (and thus averaged valence) with the relatively slow method of EPR spectroscopy (ca. 10^{-8} s) and yet demonstrate the inequivalence of CO stretching bands and thus trapped valence by IR spectroscopy, that is, on the vibrational time scale of about 10^{-13} s.[30b]



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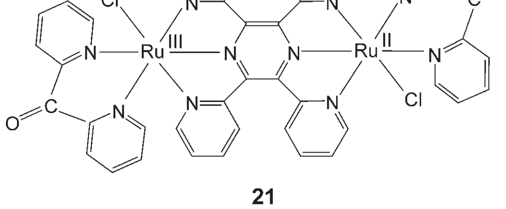
Finding appropriate conditions for IR spectroscopy is not always easy; in addition to the metal carbonyl stretching bands[29,30b,105,106] there are also organic carbonyl functions in ancillary ligands and bridging ligands that are suitable for monitoring the equivalence of the sites in a mixed-valent arrangement, as demonstrated by $[(\mu\text{-tppz})\{Ru(dpk)Cl\}_2]^{3+}$ (**21**), tppz = tetrakis(2-pyridyl)pyrazine, dpk = 2,2′-dipyridylketone.[56c]



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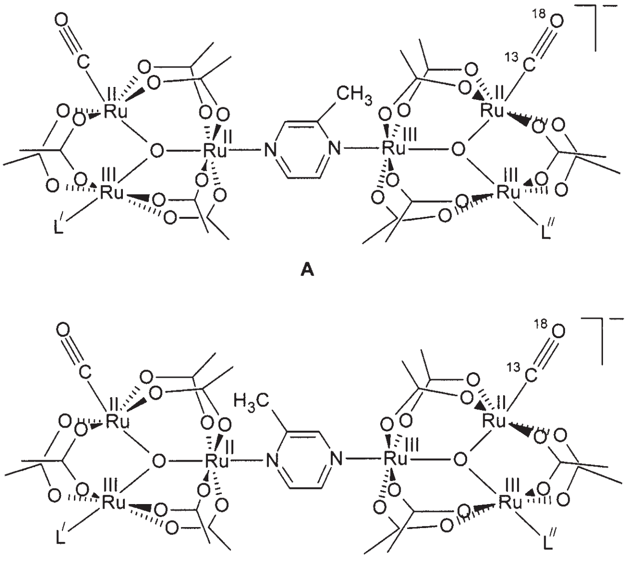
In a more sophisticated fashion, Kubiak and co-workers have established experimentally[29,33] the existence of dynamic equilibrium mixtures containing "charge-transfer isomers" of mixed-valent ruthenium complexes within the molecular frameworks of $[\{Ru_3(\mu\text{-O})(\mu\text{-CH}_3COO)_6(^{12}C^{16}O)(L')\}(\mu\text{-BL})\{Ru_3(\mu\text{-O})(\mu\text{-CH}_3COO)_6(^{13}C^{18}O)(L'')\}]$ (in which μ-BL = pyrazine derivatives) by monitoring the ν(CO) vibrations in the infrared spectra. The mixed-valent charge transfer isomers differ in the location of the odd electron, and the slightly asymmetric ligand environment around the metal centers facilitates their experimental identification.

The IR spectra of the starting compound $Ru_3^{III,III,II}$–$Ru_3^{III,III,II}$ (**22**) and doubly reduced $Ru_3^{III,II,II}$–$Ru_3^{III,II,II}$ ($\mathbf{22}^{2-}$) species exhibit two ν(CO) bands, separated by 90 cm^{-1} because of the isotope substitution of $\nu(^{12}C^{16}O)$ with $\nu(^{13}C^{18}O)$. However, the mixed-valent intermediate $Ru_3^{III,II,II}$–$Ru_3^{III,III,II}$ ($\mathbf{22}^{-}$) shows four ν(CO) bands at 1950(CO)/1861($^{13}C^{18}O$) and 1948(CO)/1859($^{13}C^{18}O$) cm^{-1} because of the presence of an equilibrium mixture of two charge-transfer isomers **A** and **B**, respectively.



22

Similar studies have also been extended to molecular frameworks with symmetrical bridging ligands, such as BL = pyrazine in combination with different ancillary ligands L′ and L″ such as 4-dimethylaminopyridine/pyridine, pyridine/4-cyanopyridine, or 4-dimethylaminopyridine/4-cyanopyridine.[29,33]

The experimental evidence for the existence of bistable mixed-valent isomers **22A** and **22B** and their switching times of about 10^{-12} s as inferred from temperature-dependent coalescence of carbonyl stretching bands may be eventually employed to provide a solid basis for the fabrication of molecular electronic devices.

3. Lessons and Outlook

The research described herein illustrates that the repertoire of novel mixed-valent complexes has not yet been exhausted, even in the seemingly well-covered[10–18] area of ruthenium chemistry. Beyond the classical textbook examples related to the Creutz–Taube ion and many other bis(pentaammineruthenium) complexes there are many remarkable, stable species accessible with unusual ligand settings whose characteristic physical properties do not always follow simple rules. However, the emergence of a fascinating coordination chemistry with non-innocent bridging ligands has raised the danger of mistaking radical complexes for mixed-valent intermediates; the experimental (EPR spectroscopy) and theoretical methodology to differentiate between these cases has been described herein.

Common misconceptions about simple relations between electrochemical results and the valence situation or between the IVCT band intensity and electronic coupling should therefore be avoided, and absent IVCT bands or EPR signals are not incompatible with a mixed-valent situation. On the other hand, near-infrared absorption bands may be misleading because radical ions and their complexes may also exhibit such NIR bands. Research areas requiring more attention are those of photophysical activity (luminescence[107]) or magnetism in ruthenium and osmium mixed-valence chemistry, both of which are influenced strongly by spin-orbit coupling effects. The extension to higher nuclearity systems (e.g. dendrimers[108]) and to main-group elements or organic analogues[25] or the study of “inverse” situations to Equation (1) (L^n-M-L^{n+1} instead of M^n-L-M^{n+1})[109,110] are developing into attractive research areas where the concepts outlined herein can be applied.

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[1] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 2213.

[2] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

[3] a) *Mixed Valency Systems—Applications in Chemistry, Physics and Biology* (Ed.: K. Prassides), Kluwer Academic Publishers, Dordrecht, **1991**; b) W. Kaim, W. Bruns, J. Poppe, V. Kasack, *J. Mol. Struct.* **1993**, *292*, 221.

[4] H. Taube, *Angew. Chem.* **1984**, *96*, 315; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 329.

[5] a) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, p. 1022; b) A. Bino, F. A. Cotton, T. R. Felthouse, *Inorg. Chem.* **1979**, *18*, 2599; c) W. Kaim, C. Titze, A. Klein, A. Knödler, S. Zalis, *Isr. J. Chem.* **2001**, *41*, 145, and references therein.; d) B. D. Yeomans, D. G. Humphrey, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1997**, 4153.

[6] a) C. Creutz, H. Taube, *J. Am. Chem. Soc.* **1969**, *91*, 3988; b) C. Creutz, H. Taube, *J. Am. Chem. Soc.* **1973**, *95*, 1086.

[7] a) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, p. 1017; b) C. Housecroft, A. G. Sharpe, *Inorganic Chemistry*, 2nd ed., Pearson, Harlow, **2005**, p. 679.

[8] V. Boekelheide, *Pure Appl. Chem.* **1986**, *58*, 1.

[9] J. Heck, G. Lange, M. Malessa, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 659.

[10] C. Creutz, *Prog. Inorg. Chem.* **1983**, *30*, 1.

[11] D. E. Richardson, H. Taube, *Coord. Chem. Rev.* **1984**, *60*, 107.

[12] R. J. Crutchley, *Adv. Inorg. Chem.* **1994**, *41*, 273.

[13] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.

[14] K. D. Demadis, D. C. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655.

[15] J.-P. Launay, *Chem. Soc. Rev.* **2001**, *30*, 386.

[16] a) M. D. Ward, *Chem. Soc. Rev.* **1995**, *24*, 121; b) J. A. McCleverty, M. D. Ward, *Acc. Chem. Res.* **1998**, *31*, 842; c) D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383.

[17] a) D. M. D’Alessandro, F. R. Keene, *Chem. Soc. Rev.* **2006**, *35*, 424; b) D. M. D’Alessandro, F. R. Keene, *Chem. Rev.* **2006**, *106*, 2270.

[18] a) J. T. Hupp in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, Amsterdam, **2003**, p. 709; b) R. J. Crutchley, in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, Amsterdam, **2003**, p. 235.

[19] a) N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391; b) N. S. Hush, *Coord. Chem. Rev.* **1985**, *64*, 135; c) C. Creutz, M. D. Newton, N. Sutin, *J. Photochem. Photobiol. A* **1994**, *82*, 47.

[20] a) V. Petrov, J. T. Hupp, C. Mottley, L. C. Mann, *J. Am. Chem. Soc.* **1994**, *116*, 2171; b) D. H. Oh, M. Sano, S. G. Boxer, *J. Am. Chem. Soc.* **1991**, *113*, 6880; c) R. C. Rocha, M. G. Brown, C. H. Londergan, J. C. Salsman, C. P. Kubiak, A. P. Shreve, *J. Phys. Chem. A* **2005**, *109*, 9006.

[21] S. Fraysse, C. Coudret, J.-P. Launay, *J. Am. Chem. Soc.* **2003**, *125*, 5880.

[22] a) M. D. Ward, *J. Chem. Educ.* **2001**, *78*, 321; b) M. D. Ward, *Chem. Ind.* **1996**, 568; c) M. D. Ward, *Chem. Ind.* **1997**, 640.

[23] S. B. Braun-Sand, O. Wiest, *J. Phys. Chem. B* **2003**, *107*, 9624.

[24] a) S. B. Braun-Sand, O. Wiest, *J. Phys. Chem. A* **2003**, *107*, 285; b) C. S. Lent, B. Isaksen, M. Lieberman, *J. Am. Chem. Soc.* **2003**, *125*, 1056.

[25] a) S. F. Nelsen, *Chem. Eur. J.* **2000**, *6*, 581; b) C. Lambert, G. Nöll, J. Schelter, *Nat. Mater.* **2002**, *1*, 69; c) J. Fiedler, S. Zalis, A. Klein, F. Hornung, W. Kaim, *Inorg. Chem.* **1996**, *35*, 3039.

[26] a) D. M. D’Alessandro, F. R. Keene, *Dalton Trans.* **2004**, 3950; b) siehe auch R. J. LeSuer, W. E. Geiger, *Angew. Chem.* **2000**, *112*, 254; *Angew. Chem. Int. Ed.* **2000**, *39*, 248.

[27] a) C. E. B. Evans, M. L. Naklicki, A. R. Rezvani, C. A. White, V. V. Kondratiev, R. J. Crutchley, *J. Am. Chem. Soc.* **1998**, *120*, 13096; b) M. Al-Noaimi, G. P. A. Yap, R. J. Crutchley, *Inorg. Chem.* **2004**, *43*, 1770.

[28] S. Berger, A. Klein, W. Kaim, J. Fiedler, *Inorg. Chem.* **1998**, *37*, 5664.

[29] a) J. C. Salsman, C. P. Kubiak, *J. Am. Chem. Soc.* **2005**, *127*, 2382; b) C. H. Londergan, C. P. Kubiak, *Chem. Eur. J.* **2003**, *9*, 5962; c) C. H. Londergan, C. P. Kubiak, *J. Phys. Chem. A* **2003**, *107*, 9301; d) C. H. Londergan, J. C. Salsman, S. Ronco, L. M.

Dolkas, C. P. Kubiak, *J. Am. Chem. Soc.* **2002**, *124*, 6236; e) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, J. Washington, C. P. Kubiak, *Science* **1997**, *277*, 660; f) C. H. Londergan, J. C. Salsman, S. Ronco, C. P. Kubiak, *Inorg. Chem.* **2003**, *42*, 926.

[30] a) A. B. P. Lever in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, Amsterdam, **2003**, p. 435; b) A. P. Meacham, K. L. Druce, Z. R. Bell, M. D. Ward, J. B. Keister, A. B. P. Lever, *Inorg. Chem.* **2003**, *42*, 7887.

[31] See, for example, G. C. Dismukes in *Mixed Valency Systems: Applications in Chemistry, Physics and Biology* (Ed.: K. Prassides), Kluwer Academic Publishers, Dordrecht, **1991**, p. 137 (NATO ACSI Series).

[32] D. A. Bardwell, L. Horsburgh, J. C. Jeffery, L. F. Joulié, M. D. Ward, I. Webster, L. J. Yellowlees, *J. Chem. Soc. Dalton Trans.* **1996**, 2527.

[33] R. J. Crutchley, *Angew. Chem.* **2005**, *117*, 6610; *Angew. Chem. Int. Ed.* **2005**, *44*, 6452.

[34] J. A. Baumann, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 345.

[35] M. L. Naklicki, R. J. Crutchley, *Inorg. Chim. Acta* **1994**, *225*, 123.

[36] S. Kar, B. Sarkar, S. Ghumaan, D. Roy, F. A. Urbanos, J. Fiedler, R. B. Sunoj, R. Jimenez-Aparicio, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2005**, *44*, 8715.

[37] Y. Hoshino, S. Higuchi, J. Fiedler, C.-Y. Su, A. Knödler, B. Schwederski, B. Sarkar, H. Hartmann, W. Kaim, *Angew. Chem.* **2003**, *115*, 698; *Angew. Chem. Int. Ed.* **2003**, *42*, 674.

[38] Y. Dong, H. Fujii, M. P. Hendrich, R. A. Leising, G. Pan, C. R. Randall, E. C. Wilkinson, Y. Zang, L. Que, Jr., B. G. Fox, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 2778.

[39] For species such as $[Ru(bpy)_3]^+$ the ruthenium(I) designation has sometimes been used, however, UV-Vis-NIR, IR/Raman, and EPR spectroscopic studies have clearly demonstrated the reduction of bpy ligand(s) in a Ru^{II} complexW. Kaim, S. Ernst, V. Kasack, *J. Am. Chem. Soc.* **1990**, *112*, 173.

[40] a) W. Kaim, *Coord. Chem. Rev.* **2001**, *219–221*, 463; b) A. Klein, V. Kasack, R. Reinhardt, T. Sixt, T. Scheiring, S. Zalis, J. Fiedler, W. Kaim, *J. Chem. Soc. Dalton Trans.* **1999**, 575.

[41] a) B. Sarkar, W. Kaim, J. Fiedler, C. Duboc, *J. Am. Chem. Soc.* **2004**, *126*, 14706; b) B. Sarkar, S. Zališ, J. Fiedler, C. Duboc, S. Roy, W. Kaim, unpublished results.

[42] a) S. Berger, A. Klein, M. Wanner, J. Fiedler, W. Kaim, *Inorg. Chem.* **2000**, *39*, 2516; b) A. Klein, S. Hasenzahl, W. Kaim, J. Fiedler, *Organometallics* **1998**, *17*, 3532.

[43] O. Renn, A. Albinati, B. Lippert, *Angew. Chem.* **1990**, *102*, 71; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 84.

[44] a) S. Patra, B. Mondal, B. Sarkar, M. Niemeyer, G. K. Lahiri, *Inorg. Chem.* **2003**, *42*, 1322; b) S. Kar, T. A. Miller, S. Chakraborty, B. Sarkar, B. Pradhan, R. K. Sinha, T. Kundu, M. D. Ward, G. K. Lahiri, *Dalton Trans.* **2003**, 2591; c) S. Kar, B. Pradhan, R. K. Sinha, T. Kundu, P. Kodgire, K. K. Rao, V. G. Puranik, G. K. Lahiri, *Dalton Trans.* **2004**, 1752.

[45] a) B. D. Yeomans, L. S. Kelso, P. A. Tregloan, F. R. Keene, *Eur. J. Inorg. Chem.* **2001**, 239; b) D. M. D'Alessandro, F. R. Keene, *Chem. Eur. J.* **2005**, *11*, 3679; c) D. M. D'Alessandro, M. S. Davies, F. R. Keene, *Inorg. Chem.* **2006**, *45*, 1656.

[46] a) S. Patra, B. Sarkar, S. Ghumaan, J. Fiedler, W. Kaim, G. K. Lahiri, *Dalton Trans.* **2004**, 754; b) S. Ghumaan, B. Sarkar, M. P. Patil, J. Fiedler, R. B. Sunoj, W. Kaim, G. K. Lahiri, unpublished results.

[47] a) N. Shan, S. J. Vickers, H. Adams, M. D. Ward, J. A. Thomas, *Angew. Chem.* **2004**, *116*, 4028; *Angew. Chem. Int. Ed.* **2004**, *43*, 3938; b) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, H. Kido, I. S. Zavarine, T. Richmond, J. Washington, C. P. Kubiak, *J. Am. Chem. Soc.* **1999**, *121*, 4625; c) K.-I. Ota, H. Sasaki, T. Matsui, T. Hamaguchi, T. Yamaguchi, T. Ito, H. Kido, C. P. Kubiak, *Inorg. Chem.* **1999**, *38*, 4070; d) K.-L. Ota, H. Sasaki, T. Matsui, T. Hamaguchi, T. Yamaguchi, T. Ito, H. Kido, C. P. Kubiak, *Inorg. Chem.* **1999**, *38*, 4070.

[48] a) A. von Kameke, G. M. Tom, H. Taube, *Inorg. Chem.* **1978**, *17*, 1790; b) N. E. Katz, C. Creutz, N. Sutin, *Inorg. Chem.* **1988**, *27*, 1687; c) C. A. Bignozzi, R. Argazzi, C. Chiorboli, F. Scandola, R. B. Dyer, J. R. Schoonover, T. J. Meyer, *Inorg. Chem.* **1994**, *33*, 1652; d) M. Sommovigo, A. Ferretti, M. Venturi, P. Ceroni, C. Giardi, G. Denti, *Inorg. Chem.* **2002**, *41*, 1263.

[49] a) M. Moscherosch, E. Waldhör, H. Binder, W. Kaim, J. Fiedler, *Inorg. Chem.* **1995**, *34*, 4326; b) E. Waldhör, W. Kaim, M. Lawson, J. Jordanov, *Inorg. Chem.* **1997**, *36*, 3248; c) S. Záliš, W. Kaim, B. Sarkar, C. Duboc, unpublished results.

[50] a) H. Krentzien, H. Taube, *J. Am. Chem. Soc.* **1976**, *98*, 6379; b) H. Krentzien, H. Taube, *Inorg. Chem.* **1982**, *21*, 4001; c) R. Gross, W. Kaim, *Inorg. Chem.* **1986**, *25*, 4865.

[51] V. C. Lau, L. A. Berben, J. R. Long, *J. Am. Chem. Soc.* **2002**, *124*, 9042.

[52] a) M. Haga, Md. M. Ali, R. Arakawa, *Angew. Chem.* **1996**, *108*, 85; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 76; b) M. Haga, Md. M. Ali, H. Sato, H Monjushiro, K. Nozaki, K. Kano, *Inorg. Chem.* **1998**, *37*, 2320.

[53] a) K. A. Goldsby, T. J. Meyer, *Inorg. Chem.* **1984**, *23*, 3002; b) F. Baumann, W. Kaim, M. Garcia Posse, N. E. Katz, *Inorg. Chem.* **1998**, *37*, 658.

[54] a) W. Kaim, V. Kasack, H. Binder, E. Roth, J. Jordanov, *Angew. Chem.* **1988**, *100*, 1229; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1174; b) V. Kasack, W. Kaim, H. Binder, J. Jordanov, E. Roth, *Inorg. Chem.* **1995**, *34*, 1924.

[55] J. Poppe, M. Moscherosch, W. Kaim, *Inorg. Chem.* **1993**, *32*, 2640.

[56] a) R. Ruminski, J. Kiplinger, T. Cockroft, C. Chase, *Inorg. Chem.* **1989**, *28*, 370; b) N. Chanda, B. Sarkar, J. Fiedler, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2004**, *43*, 5128; c) S. Ghumaan, B. Sarkar, N. Chanda, M. Sieger, J. Fiedler, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2006**, *45*, 7955.

[57] a) J.-P. Collin, P. Lainé, J.-P. Launay, J.-P. Sauvage, A. Sour, *J. Chem. Soc. Chem. Commun.* **1993**, 434; b) M. Beley, J.-P. Collin, R. Louis, B. Metz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1991**, *113*, 8521.

[58] a) J.-P. Sutter, D. M. Grove, M. Beley, J.-P. Collin, N. Veldman, A. L. Spek, J.-P. Sauvage, G. van Koten, *Angew. Chem.* **1994**, *106*, 1359; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1282; b) M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, P. Lainé, J.-P. Launay, J.-P. Sauvage, *Angew. Chem.* **1994**, *106*, 1854; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1775; c) C. Patoux, J.-P. Launay, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, S. James, J.-P. Sauvage, *J. Am. Chem. Soc.* **1998**, *120*, 3717.

[59] A. Knödler, J. Fiedler, W. Kaim, *Polyhedron* **2004**, *23*, 701.

[60] T. W. Marin, B. J. Homoelle, K. G. Spears, J. T. Hupp, L. O. Spreer, *J. Phys. Chem. A* **2002**, *106*, 1131.

[61] a) F. R. Keene, *Chem. Soc. Rev.* **1998**, *27*, 185; b) L. S. Kelso, D. A. Reitsma, F. R. Keene, *Inorg. Chem.* **1996**, *35*, 5144.

[62] a) M. Haga, T. Ano, K. Kano, S. Yamabe, *Inorg. Chem.* **1991**, *30*, 3843; b) T. E. Keyes, R. J. Forster, P. M. Jayaweera, C. G. Coates, J. J. McGarvey, J. G. Vos, *Inorg. Chem.* **1998**, *37*, 5925; c) S. Fanni, C. Di Pietro, S. Serroni, S. Campagna, J. G. Vos, *Inorg. Chem. Commun.* **2000**, *3*, 42; d) C. Di Pietro, S. Serroni, S. Campagna, M. T. Gandolfi, R. Ballardini, S. Fanni, W. R. Browne, J. G. Vos, *Inorg. Chem.* **2002**, *41*, 2871; e) R. C. Rocha, H. E. Toma, *Inorg. Chem. Commun.* **2001**, *4*, 230; f) H. Tannai, K. Tsuge, Y. Sasaki, *Inorg. Chem.* **2005**, *44*, 5206.

[63] A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, **1996**.

[64] a) S. Ernst, V. Kasack, W. Kaim, *Inorg. Chem.* **1988**, *27*, 1146; b) S. Ernst, P. Hänel, J. Jordanov, W. Kaim, V. Kasack, E. Roth, *J. Am. Chem. Soc.* **1989**, *111*, 1733.

[65] D. M. D'Alessandro, M. S. Davies, F. R. Keene, *Inorg. Chem.* **2006**, *45*, 1656.

[66] a) B. Sarkar, S. Patra, J. Fiedler, R. Sunoj, D. Janardanan, S. M. Mobin, M. Niemeyer, G. K. Lahiri, W. Kaim, *Angew. Chem.* **2005**, *117*, 5800; *Angew. Chem. Int. Ed.* **2005**, *44*, 5655; b) B. Sarkar, S. Patra, J. Fiedler, R. Sunoj, D. Janadanan, G. K. Lahiri, W. Kaim, unpublished results.

[67] W. Kaim, V. Kasack, *Inorg. Chem.* **1990**, *29*, 4696.

[68] a) G. Giuffrida, S. Campagna, *Coord. Chem. Rev.* **1994**, *135*, 517; b) R. H. Laye, S. M. Couchman, M. D. Ward, *Inorg. Chem.* **2001**, *40*, 4089.

[69] P. J. Mosher, G. P. A. Yap, R. J. Crutchley, *Inorg. Chem.* **2001**, *40*, 1189.

[70] a) P. A. Lay, R. H. Magnuson, H. Taube, *Inorg. Chem.* **1988**, *27*, 2364; b) J. M. Keane, W. D. Harman, *Organometallics* **2005**, *24*, 1786; c) S. Ye, B. Sarkar, C. Duboc, J. Fiedler, W. Kaim, *Inorg. Chem.* **2005**, *44*, 2843.

[71] a) B. Sarkar, W. Kaim, A. Klein, B. Schwederski, J. Fiedler, C. Duboc-Toia, G. K. Lahiri, *Inorg. Chem.* **2003**, *42*, 6172; b) B. Sarkar, T. Schurr, J. Fiedler, T. Varnali, O. Sarper, G. K. Lahiri, W. Kaim, unpublished results.

[72] a) W. Kaim, *Coord. Chem. Rev.* **2002**, *230*, 127; b) P. Audebert, S. Sadki, F. Miomandre, G. Clavier, M. C. Vernières, M. Saoud, P. Hapiot, *New J. Chem.* **2004**, *28*, 387.

[73] J. Sauer in *Comprehensive Heterocyclic Chemistry II*, *Vol. 6* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriver), Elsevier Science, Oxford, **1996**, p. 901.

[74] *Organic Electronics* (Ed.: H. Klauk), Wiley-VCH, Weinheim, **2006**.

[75] a) P. Bäuerle, in *Electronic Materials: The Oligometric Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**; b) R. Azumi, E. Mena-Osteritz, R. Boese, J. Benet-Buchholz, P. Bäuerle, *J. Mater. Chem.* **2006**, *16*, 728.

[76] Q. T. Zhang, J. M. Tour, *J. Am. Chem. Soc.* **1998**, *120*, 5355.

[77] a) S. Patra, B. Sarkar, S. Maji, J. Fiedler, F. A. Urbanos, R. Jimenez-Aparicio, W. Kaim, G. K. Lahiri, *Chem. Eur. J.* **2006**, *12*, 489; b) M. Haga, M. Ishizuya, T. Kanesugi, D. Sakiyama, J. Fees, W. Kaim, *Indian J. Chem. Sect. A* **2003**, *42*, 2290.

[78] P. Chaudhuri, K. Wieghardt, *Prog. Inorg. Chem.* **2001**, *50*, 501.

[79] a) M. Haga, E. S. Dodsworth, A. B. P. Lever, *Inorg. Chem.* **1986**, *25*, 447; b) C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.* **1994**, *41*, 331.

[80] a) A. Dei, D. Gatteschi, L. Pardi, *Inorg. Chem.* **1990**, *29*, 1442; b) S. Patra, B. Sarkar, S. Ghumaan, J. Fiedler, S. Zalis, W. Kaim, G. K. Lahiri, *Dalton Trans.* **2004**, 750.

[81] W. Kaim, *Coord. Chem. Rev.* **2001**, *219–221*, 463.

[82] W. Kaim, *Coord. Chem. Rev.* **1987**, *76*, 187.

[83] M. Heilmann, S. Frantz, W. Kaim, J. Fiedler, C. Duboc, *Inorg. Chim. Acta* **2006**, *359*, 821.

[84] S. Maji, B. Sarkar, S. Patra, J. Fiedler, S. M. Mobin, V. G. Puranik, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2006**, *45*, 1316.

[85] a) I. Brady, D. Leane, H. P. Hughes, R. J. Forster, T. E. Keyes, *Dalton Trans.* **2004**, 334; b) A. M. W. Cargill Thompson, J. C. Jeffery, D. J. Liard, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **1996**, 879; c) M. D. Ward, *Inorg. Chem.* **1996**, *35*, 1712; d) M. Newell, J. D. Ingram, T. L. Easun, S. J. Vickers, H. Adams, M. D. Ward, J. A. Thomas, *Inorg. Chem.* **2006**, *45*, 821; e) A. M. Barthram, Z. R. Reeves, J. C. Jeffery, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **2000**, 3162.

[86] J. A. Weil, J. T. Bolton, J. E. Wertz, *Electron Paramagnetic Resonance*, Wiley, New York, **1994**.

[87] a) C. Remenyi, M. Kaupp, *J. Am. Chem. Soc.* **2005**, *127*, 11399; b) S. Patra, B. Sarkar, S. M. Mobin, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2003**, *42*, 6469.

[88] a) S. D. Ernst, W. Kaim, *Inorg. Chem.* **1989**, *28*, 1520; b) for a discussion on organic systems: J. V. Lockard, J. I. Zink, A. E. Konradsson, M. N. Weaver, S. F. Nelsen, *J. Am. Chem. Soc.* **2003**, *125*, 13471; c) E. A. Plummer, J. I. Zink, *Inorg. Chem.* **2006**, *45*, 6556.

[89] R. W. Callahan, F. R. Keene, T. J. Meyer, D. J. Salmon, *J. Am. Chem. Soc.* **1977**, *99*, 1064.

[90] T. Scheiring, W. Kaim, J. A. Olabe, A. R. Parise, J. Fiedler, *Inorg. Chim. Acta* **2000**, *300–302*, 125.

[91] S. Ghumaan, B. Sarkar, S. Patra, J. van Slageren, J. Fiedler, W. Kaim, G. K. Lahiri, *Inorg. Chem.* **2005**, *44*, 3210.

[92] S. Kar, B. Sarkar, S. Ghumaan, D. Janardanan, J. van Slageren, J. Fiedler, V. G. Puranik, R. B. Sunoj, W. Kaim, G. K. Lahiri, *Chem. Eur. J.* **2005**, *11*, 4901.

[93] T. Fujino, Y. Hoshino, M. Eto, Y. Masuda, Y. Yukawa, J. Fiedler, W. Kaim, *Chem. Lett.* **2003**, *32*, 274.

[94] F. Hornung, F. Baumann, W. Kaim, J. A. Olabe, L. D. Slep, J. Fiedler, *Inorg. Chem.* **1998**, *37*, 311; F. Hornung, F. Baumann, W. Kaim, J. A. Olabe, L. D. Slep, J. Fiedler, *Inorg. Chem.* **1998**, *37*, 5402.

[95] M. Wanner, T. Scheiring, W. Kaim, L. D. Slep, L. M. Baraldo, J. A. Olabe, S. Zalis, E. J. Baerends, *Inorg. Chem.* **2001**, *40*, 5704.

[96] V. Kasack, B. Sarkar, W. Kaim, J. Jordanov, E. Roth, J. Fiedler, unpublished results.

[97] M. C. Barral, S. Herrero, R. Jiménez-Aparicio, M. R. Torres, F. A. Urbanos, *Angew. Chem.* **2005**, *117*, 309; *Angew. Chem. Int. Ed.* **2005**, *44*, 305.

[98] a) W. Kaim, A. Klein, M. Glöckle, *Acc. Chem. Res.* **2000**, *33*, 755; b) W. Kaim, B. Sarkar, *Coord. Chem. Rev.*, **2007**, *251*, 584.

[99] S. Chellamma, M. Lieberman, *Inorg. Chem.* **2001**, *40*, 3177.

[100] a) A. Klein, O. Lavastre, J. Fiedler, *Organometallics* **2006**, *25*, 635, and references therein.; b) G.-L. Xu, G. Zou, Y.-H. Ni, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem. Soc.* **2003**, *125*, 10057.

[101] A. Klein, C. Vogler, W. Kaim, *Organometallics* **1996**, *15*, 236.

[102] To analogous $\mathrm{Fe^{III}Fe^{II}}$ Systems: M. Glöckle, W. Kaim, N. E. Katz, M. Garcia Posse, E. Cutin, J. Fiedler, *Inorg. Chem.* **1999**, *38*, 3270.

[103] P. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439.

[104] C. S. Araujo, M. G. B. Drew, V. Felix, L. Jack, J. Madureira, M. Newell, S. Roche, T. M. Santos, J. A. Thomas, L. Yellowlees, *Inorg. Chem.* **2002**, *41*, 2250.

[105] M. H. Cheah, S. J. Borg, M. I. Bondin, S. P. Best, *Inorg. Chem.* **2004**, *43*, 5635.

[106] a) W. Bruns, W. Kaim, E. Waldhör, M. Krejcik, *Inorg. Chem.* **1995**, *34*, 663; b) W. Kaim, W. Bruns, S. Kohlmann, M. Krejcik, *Inorg. Chim. Acta* **1995**, *229*, 143.

[107] a) T. E. Keyes, B. Evrard, J. G. Vos, C. Brady, J. J. McGarvey, P. Jayaweera, *Dalton Trans.* **2004**, 2341; b) W. R. Browne, N. M. O'Boyle, W. Henry, A. L. Guckian, S. Horn, T. Fett, C. M. O'Connor, M. Duati, L. De Cola, C. G. Coates, K. L Ronayne, J. J. McGarvey, J. G. Vos, *J. Am. Chem. Soc.* **2005**, *127*, 1229.

[108] M. Marcaccio, F. Paolucci, C. Paradisi, S. Roffia, C. Fontanesi, L. J. Yellowlees, S. Serroni, S. Campagna, G. Denti, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 10081.

[109] Y. Sasaki, M. Abe, *Chem. Rec.* **2004**, *4*, 279.

[110] a) W. Kaim in *Electron and Proton Transfer in Chemistry and Biology* (Eds.: A. Müller, E. Diemann, W. Junge, H. Ratajczak), Elsevier, Amsterdam, **1992**, p. 45; b) W. Kaim, *Top. Curr. Chem.* **1994**, *169*, 231; c) W. Kaim, *Acc. Chem. Res.* **1985**, *18*, 160.