

# Exploration of Mixed-Valence Chemistry: Inventing New Analogues of the Creutz-Taube Ion

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## ABSTRACT

Starting from the Creutz-Taube ion as the prototype of a molecule-bridged mixed-valent complex, a number of related systems are presented in which the metal, the co-ligands, the molecular bridge, the d electron configuration, the medium, the charge, the coordination mode, or the nuclearity have been modified. The new mixed-valent configurations, as obtained through various chemical approaches, display different stabilities and spectroscopic characteristics in relation to the Creutz-Taube ion; the analysis of these results serves to provide a better understanding of fundamental aspects of molecule-mediated metal–metal interaction.

## Introduction and Background

Compounds with two or more centers of mixed valency<sup>1</sup> in a similar or identical setting have become the focus of recent research for a number of reasons. These include their role in biochemistry (e.g., Fe<sup>II</sup>Fe<sup>III</sup>, Mn<sup>III</sup>Mn<sup>IV</sup>, or Cu<sup>I</sup>-Cu<sup>II</sup> centers),<sup>1b,2</sup> their model character for intramolecular electron transfer,<sup>3</sup> their unusual spectroscopic properties,<sup>1,2,4</sup> their potential in molecular electronics,<sup>5</sup> and their function as test systems for theoretical approaches.<sup>4,6</sup>

The frequently used term “coupling”, used in describing the metal–metal interaction in mixed-valent compounds, can have different meanings, on the basis of either electrochemical (i), spectroscopic (ii), or magnetic measurements (iii).

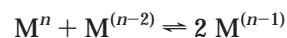
Wolfgang Kaim was born in Bad Vilbel, Germany, in 1951 and studied chemistry at the Universities of Frankfurt and Konstanz. After his doctorate in main group organometallic chemistry with Hans Bock he spent a year at Texas A&M University with F. A. Cotton in the area of metal–metal multiply bonded systems. Following his habilitation in 1982 on the coordination chemistry of reduced N-heterocycles, he developed interests in bioinorganic chemistry and (spectro)-electrochemistry and moved to a Full Professor position at the University of Stuttgart in 1987. Dr. Kaim is coauthor of an award-winning textbook on Bioinorganic Chemistry, and his main current interests include charge transfer and electron-transfer phenomena in mono- and oligonuclear coordination compounds with noninnocent ligands.

Axel Klein was born in Winnenden, Germany, and received both diploma (in 1991) and Ph.D. degrees (in 1994) from the University of Stuttgart. Since 1994 he has been developing his own research focused on organometallic complexes of the group 10 elements. His main interests lie in electrochemistry, optical spectroscopy, and EPR.

Markus Glöckle was born in Stuttgart, Germany, in 1971. He studied chemistry at the University of Stuttgart and received the diploma in 1997. Since then he has been studying complexes of copper and the group 8 elements with electron-poor N-heterocyclic ligands within the framework of his Ph.D. Thesis.

(i) The very existence of any mixed-valent “intermediate” state is quantified by the comproportionation constant  $K_c$  according to (1).<sup>7</sup>

$$K_c = 10^{\Delta E/59 \text{ mV}} = [\text{M}^{(n-1)}]^2 / [\text{M}^n][\text{M}^{(n-2)}] \quad (1)$$



$K_c$  can range from 4, the statistical value,<sup>7</sup> to more than  $10^{15}$ .<sup>5c,8</sup>

(ii) A different measure of metal–metal interaction uses information from absorption spectroscopy, specifically the energies and intensities of characteristic long-wavelength bands. For mixed-valent systems with similar or identical electron-transfer sites, these intervalence charge transfer (IVCT) transitions in a valence-localized situation (“Class II” compounds<sup>1a</sup>) may be reformulated, e.g., as  $\pi \rightarrow \pi^*$  or  $\sigma \rightarrow \sigma^*$  transitions in a fully delocalized model (“Class III” situation<sup>1a</sup>).<sup>5a,7a</sup> The latter view provides a bridge to organic species where, e.g., organodiboron or organodinitrogen radical ion intermediates with long-wavelength absorptions can be viewed as mixed-valent systems.<sup>9,10</sup> There have been various approaches to convert the spectroscopic information into electronic interaction parameters.<sup>4–7</sup>

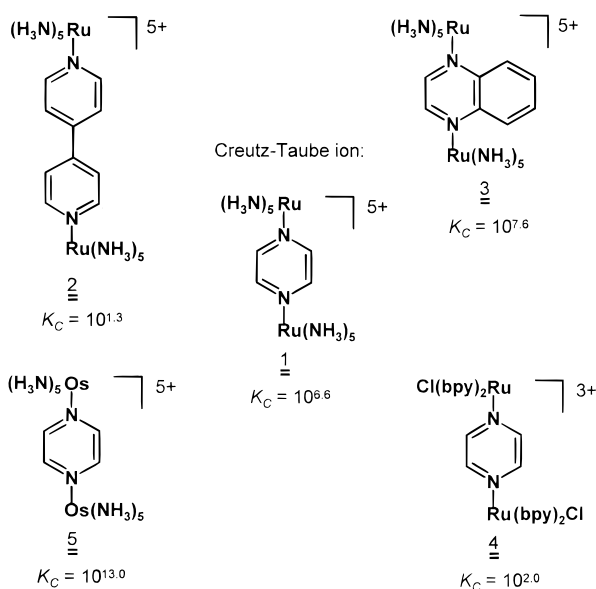
(iii) Finally, the terms “interaction” and “coupling” are also used to describe magnetic exchange in coordination compounds. Mixed-valent species can involve more than one paramagnetic metal center, such as the high-spin Fe<sup>II</sup>-Fe<sup>III</sup> sites in proteins<sup>2a,c</sup> or tetranuclear complexes  $[(\mu_4\text{-TCNX})(\text{ML}_n)_4]^k$ .<sup>11,12</sup>

While the oldest and most familiar mixed-valent coordination compound is still Prussian Blue, formulated as Fe<sup>III</sup><sub>4</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub>,<sup>13</sup> another prominent mixed-valent complex is the dinuclear Creutz-Taube ion, **1**,<sup>3,7,14</sup> which has been extensively studied both experimentally and theoretically since the 1970s.<sup>1b,3,4,6,7</sup>

**The Creutz-Taube Ion.** The Ru<sup>II</sup>Ru<sup>III</sup> mixed-valent species, **1**, was originally obtained during efforts to create coordinatively defined and kinetically stable models for degenerate inner-sphere electron transfer.<sup>3</sup> The stability of **1** is illustrated by the difference of 0.39 V between oxidation and reduction potentials (in H<sub>2</sub>O) which translates to a  $K_c$  value of more than one million.<sup>7a,14</sup> Both ruthenium centers clearly “communicate” through the bridging ligand. Secondly, **1** exhibits an intense long-wavelength absorption band in the near-infrared region at 1570 nm maximum ( $\epsilon = 5000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The intensity of that IVCT band, its low energy, and its asymmetric shape have prompted numerous efforts to calculate this feature within models involving vibronic coupling.<sup>1b,6</sup>

The lack of hyperfine coupling in the EPR spectrum<sup>15</sup> of **1** has necessitated less straightforward experimental approaches to eventually settle the question of (de)-localization of the valency; on the vibrational time scale of about  $10^{-13}$  s, the Creutz-Taube ion appears to be a delocalized species with an oxidation number of +2.5 for both metal centers.<sup>16</sup>

Chart 1



Earlier concepts and efforts to modify the Creutz-Taube ion included changes in the  $\mu\text{-}\eta^1\text{:}\eta^1$ -ligand bridge by shrinking ( $\text{N}_2$ , NCCN) or extending the pyrazine-type  $\pi$  system in various ways (**2**, **3** in Chart 1).<sup>7</sup> Co-ligands were varied to include saturated and unsaturated molecules; it was found that complexes **2** and **4** contain much weaker coupled metal centers than **1**.<sup>7,17</sup> Choosing a bis(chelate) bridging ligand ( $\mu\text{-}\eta^2\text{:}\eta^2$ ) such as 2,2'-bipyrimidine (bpy) instead of bis-monodentate pyrazine gave less impressive results at first, both with  $[\text{Ru}(\text{bpy})_2]^{2+/3+}$  or  $[\text{Ru}(\text{NH}_3)_4]^{2+/3+}$  as coordinated complex fragments (compounds **12** and **13**, cf. section C).<sup>18,19</sup> Chemically more challenging modifications of **1** required the development of advanced synthetic procedures; for instance, it took almost two decades to arrive at the very strongly coupled diosmium analogue **5** of the Creutz-Taube ion.<sup>20</sup>

**Scope of this Account.** Despite many theoretical and physical studies of **1** and related species,<sup>6,7,15–20</sup> the chemical potential springing from that discovery was not fully tapped in the early years. It is our aim to describe more recent efforts in the synthetic field, motivated by various specific questions. The scope of this article thus includes *molecule-bridged* symmetrical systems, excluding directly metal–metal bonded or atom-bridged species. To remain as close as possible to the Creutz-Taube ion situation with heteroatom donor-containing molecular bridges, we also do not cover those organometallic mixed-valent species in which the bridging ligand is coordinated through carbon atoms, e.g. bimetalloenes, bis(arene) complexes,<sup>21</sup> or  $\text{C}_n$ -bridged species.<sup>22</sup> We shall describe modifications of the bridging ligand, the coordination mode, the metals or co-ligands, the nuclearity etc., while trying to preserve as much as possible the essential features of **1**. We also tried to restrict the discussion of physical properties to an essential minimum, focusing on selected aspects as indicated in the headings **A–H**.

**A. Organometallic Analogues of the C–T Ion.** Attempts to replace the pentaammineruthenium(III,II) fragments of **1** by an organometallic  $d^5/d^6$  system failed initially because of the substitutional lability and high potential of  $d^5$  forms such as  $(\text{OC})_5\text{M}^+$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) or  $(\text{C}_5\text{R}_5)(\text{OC})_2\text{Mn}^+$ .<sup>23,24</sup> However, using the more electron-rich fragments  $(\text{R}_3\text{P})_2(\text{OC})_3\text{M}$ ,  $\text{M} = \text{Mo}, \text{W}$ , it was possible to isolate and study monocationic mixed-valent compounds **6a, b** with the pyrazine bridge.<sup>25,26</sup> They revealed  $K_c$  values and IVCT absorption features not very different from those of **1** or **5**, respectively. However, EPR data clearly showed partial spin transfer to the covalently bonded co-ligands<sup>26</sup>—an effect that is absent in **1**.<sup>15</sup>

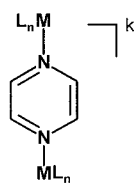
Another organometallic analogue, **7**, with  $\text{Os}^{\text{II}}\text{Os}^{\text{III}}$  configuration<sup>27</sup> is discussed below (section B) as are bis(chelate)-bridged systems (compound **15**, cf. section C).<sup>28</sup> In all instances,<sup>25–28</sup> the carbonyl-stretching features of the infrared spectra measured in nonpolar solvents revealed full delocalization of the mixed-valent states which exhibit only one, shifted, set of bands, i.e., valence averaging on the vibrational time scale.<sup>29</sup> In the localized situation as observed, e.g., for a tetracarbonyldimanganese(II,I) species with a fulvalenyl bridge,<sup>21</sup> one would expect two sets of bands close to the energies of the fully reduced and fully oxidized states, respectively.

Although they are not strictly organometallic compounds, the reviewed<sup>5c</sup> molecule-(L-)-bridged mixed-valent species  $[(\eta^3\text{-X})(\text{NO})\text{ClMo}(\mu\text{:}\eta^1, \eta^1\text{-L})\text{MoCl}(\text{NO})(\eta^3\text{-X})]^k$ ,  $\eta^3\text{-X} =$  substituted trispyrazolylborate,<sup>5a,c</sup> deserve mentioning at this point because of the low-valence combination  $\text{Mo}^{\text{II}}\text{-Mo}^{\text{I}}$  ( $d^6/d^5$ ), the low overall charge  $k = 1-$ , and the unusually large  $K_c$  values (up to  $10^{24}$  for  $\text{L} =$  pyrazine) which indicate very strong metal–metal interaction (class III behavior).<sup>5c</sup> Remarkably, the pyrazine system exhibits class I behavior for the accessible  $d^5/d^4$  state ( $k = 1+$ ).

**B. The Role of the Environment: Co-ligands, Charge and Solvent Effects.** The influence of the environment on either localization (“charge trapping”) or delocalization of valencies in mixed-valent compounds has been extensively discussed.<sup>30</sup> The sensitivity of the IVCT band to solvent variation has thus become an accepted criterion for the assignment of the “Class II” (strong solvent sensitivity) or “Class III” (solvent insensitivity) label to a mixed-valent compound.<sup>7a</sup> The Creutz-Taube ion, for instance, exhibits little such solvent effect which holds also for the  $K_c$  value; it increases only from  $10^{6.6}$  to  $10^{7.3}$  on going from the aqueous medium to, e.g., acetonitrile solution.<sup>30b</sup>

A totally different situation was found for the pyrazine-bridged bis(pentacyanoiron) analogue **8**. In water, the mixed-valent state was long known to be weakly coupled with a low-intensity IVCT band at about 1300 nm.<sup>31</sup> Recent investigations in acetonitrile and other aprotic solvents showed a much increased stability (Chart 2) and an intense, asymmetric IVCT band at 2475 nm.<sup>32</sup> Infrared spectroelectrochemistry of the CN stretching vibrations revealed a borderline situation with evidence for both localization and delocalization on the vibrational time scale (partial band averaging at ambient tempera-

Chart 2



Compd.	ML <sub>n</sub>	k	log K <sub>C</sub>	ref.
<u>1</u>	Ru(NH <sub>3</sub> ) <sub>5</sub>	5+	6.6 <sup>b</sup>	14
<u>5</u>	Os(NH <sub>3</sub> ) <sub>5</sub>	5+	13.0 <sup>b</sup>	20
<u>6a<sup>a</sup></u>	Mo(CO) <sub>3</sub> (PR <sub>3</sub> ) <sub>2</sub>	1+	6.4 <sup>c</sup>	26
<u>6b<sup>a</sup></u>	W(CO) <sub>3</sub> (PR <sub>3</sub> ) <sub>2</sub>	1+	11.0 <sup>c</sup>	26
<u>7<sup>a</sup></u>	Os(CO)(H)Cl(PR <sub>3</sub> ) <sub>2</sub>	1+	4.3 <sup>c</sup>	27
<u>8</u>	Fe(CN) <sub>5</sub>	5-	1.9 <sup>b</sup>	31
<u>8</u>	Fe(CN) <sub>5</sub>	5-	6.5 <sup>c</sup>	32
<u>9</u>	Ru(CN) <sub>5</sub>	5-	4.7 <sup>c</sup>	34
<u>10</u>	Os(CN) <sub>5</sub>	5-	5.8 <sup>c</sup>	35

<sup>a</sup> R = isopropyl

<sup>b</sup> In aqueous medium

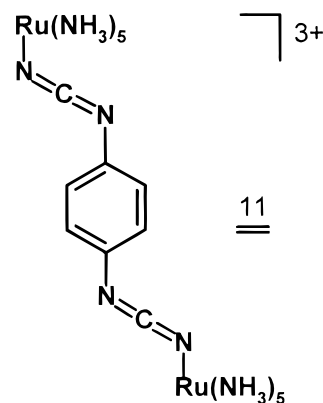
<sup>c</sup> In aprotic medium

ture). A similar situation has been reported recently<sup>33</sup> for diosmium analogues of compound **4**. The emergence and disappearance of a pyrazine ring vibrational band at about 1595 cm<sup>-1</sup> on going from the Fe<sup>II</sup>Fe<sup>II</sup> through the Fe<sup>II</sup>Fe<sup>III</sup> to the Fe<sup>III</sup>Fe<sup>III</sup> state suggests a loss of inversion symmetry and thus an at least partially localized situation in the intermediate **8**,<sup>32</sup> according to the selection rules for infrared spectroscopy, the transition must be accompanied by a dipole moment change to be observed.

Similar conclusions from the same type of reasoning have been reached for the diruthenium **9**<sup>34</sup> and the diosmium analogue **10**.<sup>35</sup> The IR spectroscopic features at 1590 cm<sup>-1</sup> solely for the mixed-valent forms **9** and **10** (indicating molecular asymmetry and thus valence localization), and the unexpectedly low and rather close K<sub>C</sub> values illustrate the crucial, leveling role of the π-acidic cyanide co-ligands.<sup>34,35</sup> In the pentaamminemetal series with truly innocent NH<sub>3</sub> co-ligands, there is a huge K<sub>C</sub> difference between the diruthenium system **1** and the diosmium analogue **5**.<sup>20</sup> Competition from the cyanide ligands for metal d electrons diminishes the extent of metal-metal interaction via the pyrazine bridge; the "Class II" character of **9** is evident from the very broad, symmetrical IVCT band at 1760 nm. The dramatic solvent effects for anions such as **8** are mirrored by effects observed for bis(pentaammineruthenium) cations such as **11** with 1,4-dicyanamidobenzenes as π-donor bridging ligands (cf. section E).<sup>36</sup> Changes in the reorganization energy as well as electrostatic and ion-pairing effects in highly charged species may be responsible for these pronounced solvent effects (Chart 3).

To complete a series (**5**, **7**, and **10**) of pyrazine-bridged diosmium(III,II) species with very different sets of co-ligands (Chart 2), we have managed to study the sparingly soluble **7** in dichloromethane.<sup>27</sup> In contrast to the common wisdom that delocalization must be associated with large K<sub>C</sub> values, this mixed-valent ion has a K<sub>C</sub> value of only 10<sup>4.3</sup> but exhibits a delocalized situation, as evident from IR

Chart 3



$$K_C = 10^{1.0} \quad (\text{H}_2\text{O})$$

$$K_C = 10^{4.8} \quad (\text{CH}_3\text{CN})$$

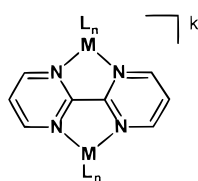
spectroelectrochemistry. Obviously, the splitting of redox potentials and the localization of charge are two separate phenomena which depend strongly, but not uniformly, on the interaction of the metal and its co-ligands with the environment.

### C. Geometry Effects: Chelate-Controlled Orientation Between the Metal Centers and the Conjugated Bridge.

Almost all early efforts to modify the C-T ion involved bis-monodentate ligands.<sup>7</sup> However, the specific correlations and conclusions derived for this vast number of compounds apply only within that class, and different coordination situations were indeed shown to exhibit different patterns.<sup>37</sup>

The first attempts to use bis(chelate) ligands such as 2,2'-bipyrimidine, e.g., in compounds **12**,<sup>18</sup> **13**,<sup>19</sup> or **14**,<sup>38</sup> met with disappointing results with regard to K<sub>C</sub> (small) and IVCT transition bands (not found). The reinvestigation of these species under different (i.e., aprotic) conditions,<sup>39,40</sup> the use of novel bridging bis(chelate) ligand systems,<sup>37,40,41</sup> and the use of organometallic species such as valence-delocalized **15**<sup>28</sup> helped to clarify the situation (Chart 4).

Chart 4



Compd.	ML <sub>n</sub>	k	log K <sub>C</sub>	ref.
<u>12</u>	Ru(bpy) <sub>2</sub>	5+	3.2 <sup>b,c</sup>	18,48
<u>13</u>	Ru(NH <sub>3</sub> ) <sub>4</sub>	5+	3.2 <sup>b</sup>	19
<u>13</u>	Ru(NH <sub>3</sub> ) <sub>4</sub>	5+	5.1 <sup>c</sup>	39
<u>14</u>	Fe(CN) <sub>4</sub>	3-	2.4 <sup>b</sup>	38
<u>14</u>	Fe(CN) <sub>4</sub>	3-	6.4 <sup>c</sup>	40
<u>15<sup>a</sup></u>	Mo(CO) <sub>2</sub> (PR <sub>3</sub> ) <sub>2</sub>	1+	8.8 <sup>c</sup>	28
<u>37</u>	PtMes <sub>2</sub>	1+	<1 <sup>c</sup>	59

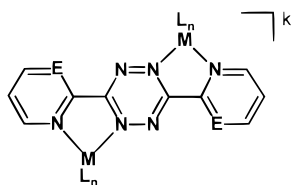
<sup>a</sup> R = n-butyl

<sup>b</sup> In aqueous medium

<sup>c</sup> In aprotic medium

As an extremely efficient metal-metal coupling class of organic acceptor ligands,<sup>8</sup> we also employed 1,2,4,5-tetrazine derivatives. While binding two metal centers in the 1,4 position at a distance of about 7 Å,<sup>42</sup> as in a

Chart 5



Compd.	ML <sub>n</sub>	k	E	log K <sub>c</sub>	ref.
<u>16</u>	Ru(NH <sub>3</sub> ) <sub>4</sub>	5+	CH	15.0 <sup>b</sup>	37a
<u>17</u>	Fe(CN) <sub>4</sub>	3-	CH	14.6 <sup>c</sup>	40
<u>18</u>	Fe(CN) <sub>4</sub>	3-	N	14.1 <sup>c</sup>	41
<u>19</u>	Ru(bpy) <sub>2</sub>	5+	N	>8.0 <sup>c</sup>	43
<u>23</u>	Ru(bpy) <sub>2</sub>	5+	CH	8.5 <sup>c</sup>	48
<u>38</u>	PtMes <sub>2</sub>	1+	CH	1.8 <sup>c</sup>	60

<sup>b</sup> In aqueous solution

<sup>c</sup> In aprotic solution

pyrazine-bridged situation, the tetrazines have an extremely low-lying  $\pi^*$  orbital ( $a_u$ ) which is localized at the four nitrogen centers.<sup>43</sup> Bis(chelating) 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) was thus shown to form not only a (ligand-)reduced paramagnetic state with two tetraammineruthenium(II) fragments but also a corresponding Ru<sup>III</sup>Ru<sup>II</sup> mixed-valent species, **16**, with the extremely high  $K_c$  value of  $10^{15.0}$ .<sup>37a</sup> Such values were previously only approached in systems bridged by ligands such as NCCN, NC-(R)C<sup>-</sup>-CN or *p*-benzoquinonediimines.<sup>7</sup> Yet despite the enormous  $K_c$  value, the IVCT band of **16** is 10 times weaker than the corresponding feature in the Creutz-Taube ion although it occurs at about the same energy with comparable asymmetric shape.<sup>37a</sup> It was thus plausible to conclude that the rigid chelate situation in **16** enforces a conformation which is not as optimal for  $d/\pi^*/d$  overlap and thus for IVCT transition intensity as that in **1** and related species with their little restricted rotation around the metal–ligand bonds (Chart 5).

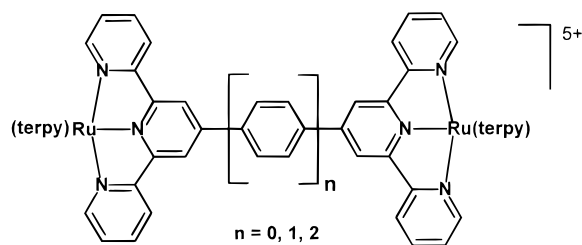
Several examples of ammineruthenium (**13**),<sup>39</sup> cyanoiron (**14**, **17**, **18**),<sup>32,40,41</sup> or bis(bipyridine)ruthenium compounds (**19**)<sup>43</sup> and organometallic analogues such as **15**<sup>28</sup> have confirmed this typical low-intensity IVCT feature of  $d^5/d^6$  mixed-valent systems bridged by bis(bidentate) acceptor ligands.

Bis(tridentate) bridging ligands, as in **20** (Chart 6), with fairly rigid configurations at the metal centers exhibit small  $K_c$  values and IVCT bands of intermediate intensity;<sup>44</sup> in contrast, cyclometalated variants (with  $\pi$  donor bridges, cf. section E) have very intense IVCT bands ( $\epsilon > 20\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) but still rather small  $K_c$  values,  $K_c < 10^3$ .<sup>45</sup>

An unusual bis(macrocyclic) diiron complex with a conjugated bis(tetradentate) ligand bridge exists in rigid **21**, causing both a large  $K_c$  and a very intense IVCT band (Chart 7).<sup>46</sup>

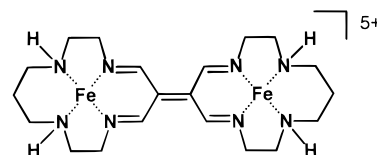
Summarizing, the relation between  $K_c$  and the intensity of the IVCT band is highly variable, depending strongly on the configuration between the bridging ligand and the metal complex fragments.

Chart 6



20

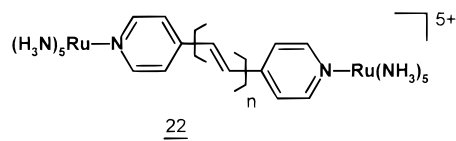
Chart 7



21  $K_c = 10^{11}$

**D. Improving on the Efficiency of the Molecular Bridge. Does the Metal–Metal Distance Matter?** It has been a basic tenet held in mixed-valence chemistry that the metal–metal interaction is largely determined by the metal–metal distance,  $d$ .<sup>1,4,6,7</sup> Using a series of related bridging ligands for bis(pentaammineruthenium(III,II)) compounds **22** or similar species, it was thus possible to obtain correlations between  $d$  and various coupling parameters, including  $K_c$  (Chart 8).<sup>5c,45,47</sup>

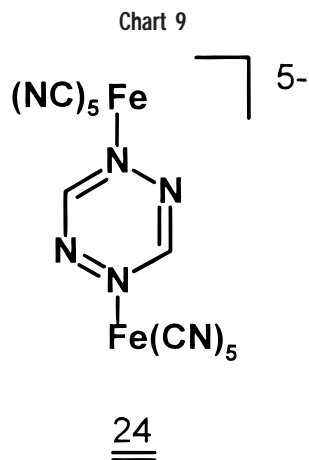
Chart 8



22

The simple lengthening of conjugated chains, however, also implies decreasing MO coefficients at the coordinated atoms of the orbital mediating the metal–metal interaction ( $\pi$  dilution effect) and thus a diminished orbital overlap at this “metal–ligand interface”. It was thus shown that within series of closely related systems, such as **14**, **17**, and **18**<sup>40</sup> or **12**, **19**, **23**, and **28**,<sup>48</sup> it is possible to have small metal–metal interaction over short distances (weakly coupling ligands) and strong metal–metal interaction over longer distances (efficiently coupling ligands).

A typical such example<sup>40</sup> involves compound **14** ( $K_c = 10^{6.4}$ ) with bpym as a ligand that allows for a metal–metal distance of about  $5.5\text{ \AA}$ <sup>49</sup> and complexes **17** or **18** ( $K_c > 10^{14}$ ) with strongly coupling tetrazine ligands which, however, keep metals at about  $7\text{ \AA}$  apart.<sup>43</sup> The extraordinary stabilization of mixed-valent states by bridging tetrazine ligands was recently demonstrated through complex **24**.<sup>8</sup> All evidence including Mössbauer data show **24** to be fully delocalized (Chart 9).

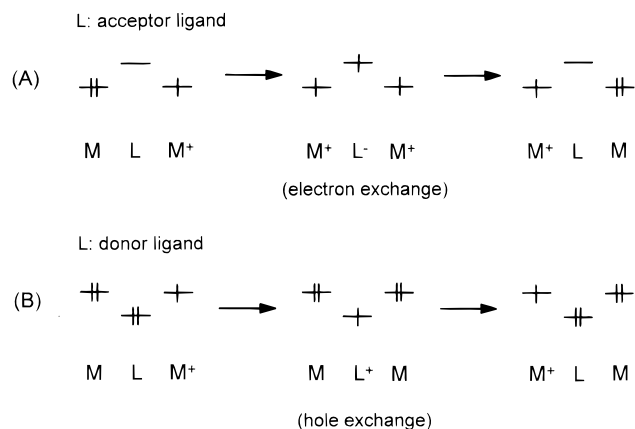


$$K_C = 10^{19} (\text{CH}_3\text{CN})$$

$$K_C \approx 10^8 (\text{H}_2\text{O})$$

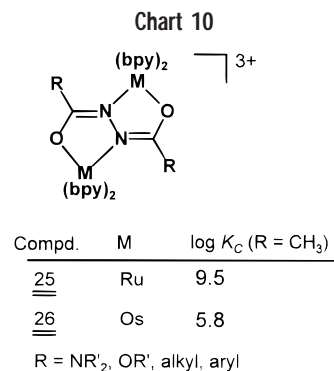
Since most  $\pi$  systems follow simple rules with regard to alternancy of bond parameters and substitution patterns, a successful correlation could be elaborated by Richardson and Taube for bis(pentaammineruthenium) mixed-valent systems with dicyanoarene bridging ligands.<sup>7b,50</sup> When choosing bridging ligands for effective metal–metal coupling, one should thus look at the  $\pi$  character (donor or acceptor, see below), the suitable coordination mode (section C), and the energy and nodal properties of the mediating orbital. The correlation with the metal–metal distance is valid only within series of directly analogous ligands.

**E. Hole vs Electron Exchange Mechanism.** The established concept of electronic interaction in the Creutz-Taube ion involves the low-lying  $\pi^*$  MO of the bridging ligand for providing a communication pathway between the metal centers (electron exchange, Figure 1A).<sup>6,7,14</sup> However, the underlying metal–ligand–metal three-center model does not necessarily have to invoke a  $\pi$ -accepting bridge, it may also be applied to mixed-valent systems in which metal–metal communication occurs via a  $\pi$  donor bridge (hole exchange alternative, Figure 1B).<sup>51</sup>

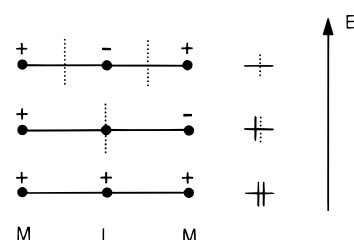


**FIGURE 1.** Electron transfer (A) and hole transfer (B) mechanism for valence exchange in symmetrically dinuclear complexes  $[\text{M}-\text{L}-\text{M}]^+$ .

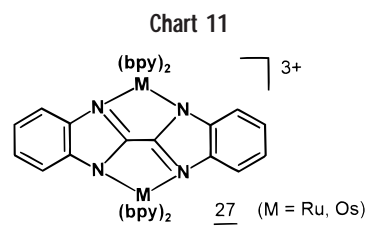
The physical and chemical consequences of this alternative can be very different, as outlined in the following.<sup>51,53</sup> Bridging two bis(2,2'-bipyridine)-ruthenium or -osmium centers via bis(chelating) 1,2-diacylhydrazido (i.e., reduced azodicarbonyl) ligands yields redox systems with stable ( $K_C > 10^5$ ) and isolable odd-electron intermediates, **25** and **26**, which show signs of dimetal(III,II) mixed-valence by XPS, UV/Vis/NIR, and EPR spectroscopy (Chart 10).<sup>53</sup>



However, the strong dependence of the EPR response on substitution effects in the bridging ligand implies significant participation of that  $\pi$  system in the spin distribution. Applying a three-center model,<sup>51</sup> we can account for this difference in a donor-bridged system relative to acceptor-bridged species by increasing the electron count from three to five (Figure 2, Chart 11). Whereas acceptor-bridged systems have a nonbonding orbital singly occupied which is distinguished by lack of contributions from the central component in the three-center model, the donor-bridged species have the unpaired electron in the uppermost, antibonding MO which contains large contributions from the bridge. Accordingly, mixed-valent systems with predominantly  $\pi$ -donor bridging ligands such as diacylhydrazido (**25**, **26**), bis(benzimidazolone) (**27**),<sup>52</sup> 1,4-dicyanamidobenzene (**11**),<sup>56</sup> or cyclometalated bis(tridentate) ligands<sup>45</sup> should generally



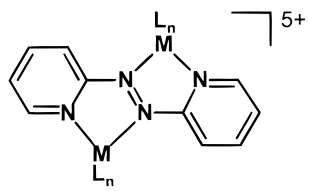
**FIGURE 2.** Orbital composition for a three component model M–L–M (left) and mixed-valency alternatives with occupation by 3 electrons (L: acceptor, metal-centered SOMO) or 5 electrons (L: donor, metal/ligand-mixed SOMO).



show a larger degree of bridge participation at the singly occupied MO.

An important consequence of the difference in situations A and B in Figure 1 is the reversed effect<sup>51</sup> on using ruthenium or osmium. In the acceptor-bridged situation where the stronger  $\pi$  donor capacity of Os<sup>II</sup> (5d<sup>6</sup>) vs Ru<sup>II</sup> (4d<sup>6</sup>) is the dominating effect, the stability of the mixed-valent form as measured by  $K_c$  is larger for 5d<sup>5</sup>/5d<sup>6</sup> species such as **5**, **6b**, or **29** relative to those of the analogous 4d<sup>5</sup>/4d<sup>6</sup> systems **1**, **6a**, and **28**, respectively (Chart 12).<sup>26,51</sup> Conversely, with bridging  $\pi$  donors, such as the 1,2-diacylhydrazido(2-) ligands, the stronger  $\pi$ -acceptor nature of Ru<sup>III</sup> vs Os<sup>III</sup> leads to larger  $K_c$  values for the diruthenium(III,II) analogues **25** relative to the corresponding diosmium(III,II) species, **26**.<sup>51</sup>

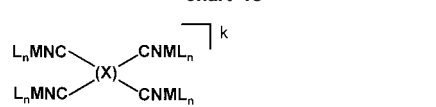
Chart 12



Compd.	ML <sub>n</sub>	log $K_c$
<u>28</u>	Ru(bpy) <sub>2</sub>	9.3
<u>29</u>	Os(bpy) <sub>2</sub>	>20

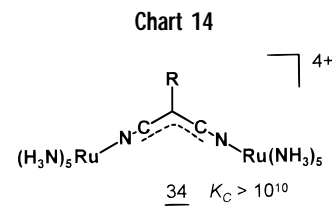
**F. Mixed Valency in Systems of Higher Nuclearity.** Mixed valency in coordination chemistry is by no means restricted to dinuclear complexes; there are molecule-bridged cluster compounds reported.<sup>29</sup> Retaining the pentaammineruthenium(III,II) metal fragment feature of **1**, we have used the potentially tetradentate TCNX acceptor ligands<sup>11,12,54</sup> to prepare a number of tetranuclear complex ions  $\{(\mu_4, (\eta^1)_4\text{-TCNX})([\text{Ru}(\text{NH}_3)_5]_4)\}^{8+}$  (**30–33**) (Chart 13).<sup>11,55</sup>

Chart 13



Compd.	ML <sub>n</sub>	k	X	(TCNX)
<u>30</u>	Ru(NH <sub>3</sub> ) <sub>5</sub>	8+		(TCNE)
<u>31</u>	Ru(NH <sub>3</sub> ) <sub>5</sub>	8+		(TCNQ)
<u>32</u>	Ru(NH <sub>3</sub> ) <sub>5</sub>	8+		(TCNB)
<u>33</u>	Ru(NH <sub>3</sub> ) <sub>5</sub>	8+		(TCNP)
<u>35</u>	Os(CO)(H)Cl(PR <sub>3</sub> ) <sub>2</sub>	0		(TCNQ)
<u>36</u>	Os(CO)(H)Cl(PR <sub>3</sub> ) <sub>2</sub>	0		(TCNB)

We could show that the TCNE and TCNQ compounds can be described as containing two intramolecularly connected delocalized Ru<sup>II</sup>Ru<sup>III</sup> entities,<sup>55</sup> each of which correspond to the malonodinitrilato-bridged mixed-valent compounds **34** reported by Krentzien and Taube (Chart 14).<sup>56</sup>

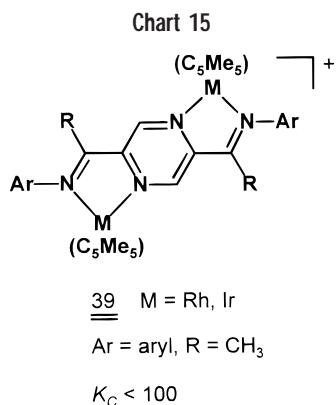


Weak intramolecular coupling of the strongly coupled dinuclear entities is evident from two-electron oxidation processes; the stepwise two-electron reduction, on the other hand, involves a mainly TCNX-based orbital. Use of the less  $\pi$ -accepting TCNB (1,2,4,5-tetracyanobenzene) or TCNP (1,2,4,5-tetracyanopyrazine) ligands yields similar results; a continuum exists between the (TCNX<sup>2-</sup>)(Ru<sup>II</sup>Ru<sup>III</sup>)<sub>2</sub> and (TCNX<sup>0</sup>)Ru<sub>4</sub><sup>II</sup> formulations for the (8+) state. In all instances and even with XPS as a very “rapid” probe, we observed equivalence for all four bound pentaammineruthenium moieties.<sup>55</sup> In a considerable change of the overall charge and polarity, the substitution of charged [Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> by neutral Os(PR<sub>3</sub>)<sub>2</sub>(CO)(H)Cl was achieved; however, the results for the electrochemical response and spectroscopy of tetranuclear compounds such as **35** or **36** are very similar to those of **31** and **32**.<sup>57</sup>

**G. Other d<sup>n</sup>/d<sup>n+1</sup> Combinations than d<sup>5</sup>/d<sup>6</sup>.** Dinuclear mixed-valent compounds with pyrazine and related bridging ligands were mainly produced with d<sup>5</sup>/d<sup>6</sup> metal centers such as Ru<sup>II</sup>Ru<sup>III</sup>,<sup>7,17,29,34</sup> Fe<sup>II</sup>Fe<sup>III</sup>,<sup>31,32</sup> Os<sup>II</sup>Os<sup>III</sup>,<sup>20,27,35</sup> Mo<sup>0</sup>Mo<sup>I</sup>,<sup>5c,25,26</sup> or W<sup>0</sup>W<sup>I</sup>.<sup>26</sup> Other combinations such as d<sup>I</sup>/d<sup>2</sup> in Mo<sup>IV</sup>Mo<sup>V</sup> species were also reported.<sup>5c</sup> The possibility of using bis(bidentate) bridging ligands with widely variable capacity for mediating metal–metal interaction has recently prompted the preparation of organometallic precursor molecules with Pt<sup>II</sup>, Rh<sup>I</sup>, or Ir<sup>I</sup>, i.e., d<sup>8</sup> centers. The presence of sterically protecting co-ligands such as shielding C<sub>5</sub>Me<sub>5</sub> or axially protecting mesityl allows for reversible one-electron oxidation to corresponding d<sup>7</sup> states. As a particularly revealing example, the use of dimesitylplatinum has allowed us to study the electrochemically reversible Pt<sup>II</sup> → Pt<sup>III</sup> transition because two axially protecting mesityl substituents prevent the coordinatively unsaturated metal center from being attacked by nucleophiles after one-electron oxidation.<sup>58</sup> Bridging two such fragments with 2,2'-bipyrimidine (bpym) did not produce any detectable splitting of the potentials of the reversible Pt<sup>II</sup>/Pt<sup>III</sup> waves; hence, a mixed-valent intermediate, **37**, could not be detected.<sup>59</sup> Only with bptz, one of the superior bridging tetrazine ligands,<sup>37,40</sup> a small splitting of potentials becomes visible in the corresponding Pt<sub>2</sub><sup>III,II</sup> mixed-valent state, **38**, corresponding to a  $K_c$  value of 70 (Charts 4 and 5).<sup>60</sup> This very small interaction between the metal centers across the bridging ligand is the result of a mismatch of participating orbitals: The oxidation of the 5d<sup>8</sup> species Pt<sup>II</sup> probably involves a d<sub>o</sub> orbital like d<sub>z<sup>2</sup></sub> which does not profit from interaction with low-lying  $\pi^*$  MOs of the acceptor bridges. In contrast, the d<sub>xz</sub> orbital of d<sup>5</sup>/d<sup>6</sup> centers in approximately octahedral conformation is of  $\pi$  symmetry which is well suited for an intermediate-stabilizing metal–ligand interaction. The cases of Rh<sub>2</sub><sup>II,I</sup>

and Ir<sub>2</sub><sup>III,I</sup>, (d<sup>7</sup>/d<sup>8</sup>) mixed-valent intermediates in pyrazine ligand-bridged situations, are discussed in the following.

**H. Outlook: Mixed Valency in Electron and Atom Transfer—Extending the Coupling Concept from Electron Transfer to Reaction Centers.** Although stable mixed-valent compounds have attracted the attention of chemists with interest in unusual new materials,<sup>1,5</sup> the coupling of mere electron-transfer processes via bridging ligands may not be sufficient to draw attention from a wider chemical community. However, if the electron transfer is coupled with atom transfer in redox *reaction centers*, the interaction of such sites and their involvement in chemical conversion may produce new phenomena, related to multielectron transfer and catalysis. Using the kinds of bridging ligands and the general approach of mixed-valent coordination chemistry related to studies of the Creutz-Taube ion, it was recently demonstrated that organometallic ECE or EEC reaction centers, [(η<sup>n</sup>-C<sub>n</sub>R<sub>n</sub>)-XM]<sup>+</sup> (M = Rh, Ir, Os; X = halogen; n = 5 or 6), which are known from hydride transfer catalysis<sup>61</sup> can be coupled by symmetrical molecular bridges such as bpym or bptz to exhibit various effects of ligand-mediated communication.<sup>62–64</sup> These effects include the splitting of two-electron processes and the occurrence of electron reservoir behavior:<sup>5b</sup> The π system of the bridging ligand is able to store one electron without affecting metal-based reactivity. However, the second added electron will then combine with the first one to cause the opening of a coordination site at the metal through chloride dissociation.<sup>62–64</sup> Related to the topic of this article and to current research,<sup>64</sup> the coupling of two equivalent ECE reaction sites through a bridging π acceptor ligand results in a splitting of the chemical steps, C, associated with the electron transfer E in EC, EEC, or ECE processes. Such a behavior is reminiscent of the much more elementary splitting of electron-transfer steps, quantified by K<sub>c</sub> in eq 1. Remarkably, in some cases, these intricate sequences involve also classical mixed-valence situations, such as **39**, with small K<sub>c</sub> values but well-detectable IVCT bands in the near-infrared (Chart 15).<sup>62,64</sup>



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