Comparison of Metal−Metal Electronic Interactions in an Isomeric Pair of Dinuclear Ruthenium Complexes with Different Bridging Pathways: Effective Hole Transfer through a Bis-phenolate Bridge

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Introduction

Dinuclear complexes in which a strong electronic interaction between redox-active metal centers affords a stable mixed-valence (MV) state are of particular interest for (i) the fundamental study of electron transfer under carefully controlled conditions and (ii) development of "molecular wires" in which electrons can be transported over long distances for possible use in molecular-scale electronic devices.[1−3] To achieve a strong electronic interaction it is necessary to match the energy of the metal-based redox orbital with an appropriate bridging ligand (BL) orbital, such that delocalization in the MV state can be optimized by a superexchange process involving the bridging ligand: either hole transfer through the BL HOMO (Figure 1a) or electron transfer through the BL LUMO (Figure 1b).[4]

The importance of this is illustrated by recent studies on complexes such as **I** [two Mo(V) centers connected by a 4,4′-bis-phenolate bridge][5,7] and **II** [two Mo(I) centers connected by a 4,4′-bipyridyl bridge].[6,7] Both undergo metal-centered oxidation and reduction processes such that two mixed-valence states are accessible for each, viz., $[\mathbf{I}]^+$, Mo(V)/Mo(VI), and $[\mathbf{I}]^-$, Mo(IV)/Mo(V); $[\mathbf{II}]^+$, Mo(I)/Mo(II), and $[\mathbf{II}]^-$, Mo(0)/

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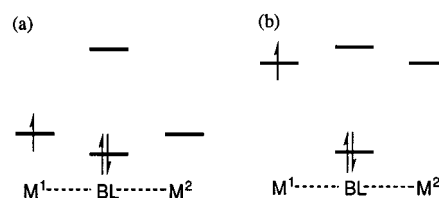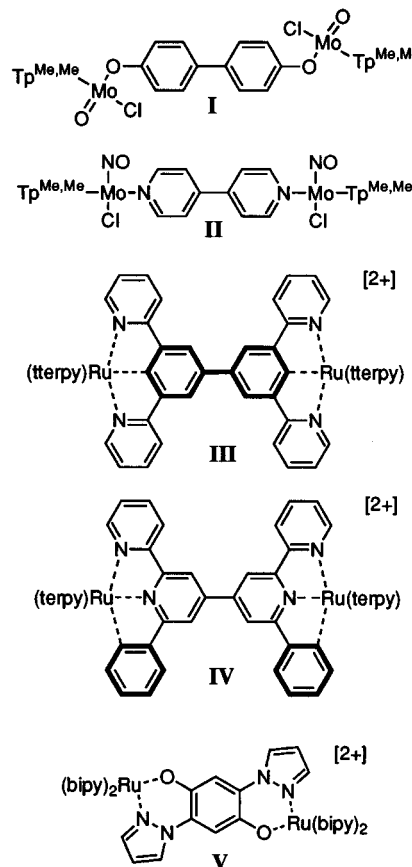(7) McCleverty, J. A.; Ward, M. D. *Acc. Chem. Res.* **1998**, *31*, 842.

Figure 1. Simple orbital diagrams showing the situations necessary for delocalization of metal-based mixed-valence states by (a) hole transfer through the HOMO of the bridging ligand and (b) electron transfer through the LUMO of the bridging ligand.

Mo(I). Complex **I** corresponds to the situation of Figure 1a, where the BL orbitals are relatively high in energy because of the double negative charge. The oxidized MV complex $[\mathbf{I}]^+$ can be delocalized by hole transfer through the BL HOMO, because the ligand-oxidized canonical form M−L$^+$−M is close in energy to the metal-oxidized form M$^+$−L−M: this is consistent with the fact that para-substituted bis-phenolates are readily oxidizable to semiquinones and then quinones. For the reduced MV state M$^-$−L−M this is less likely: hole transfer through the BL HOMO would require conversion of M$^-$−L−M to M$^-$−L$^+$−M$^-$, which is highly endergonic because of the additional charge separation involved. The more natural delocalization pathway for $[\mathbf{I}]^-$ would be electron transfer via the BL LUMO (M$^-$−L−M → M−L$^-$−M), but the high energy of the BL LUMO prevents this. The result is that successive Mo(V)/Mo(VI) couples are separated by 480 mV (corresponding to a comproportionation constant K_c of ca.10^8 for $[\mathbf{I}]^+$) whereas the two Mo(V)/Mo(IV) couples are essentially coincident, *despite the same metal fragment and the same bridging ligand being involved in each case.* Exactly opposite behavior is shown by

Scheme 1. Syntheses of H_2L^1 and H_2L^2
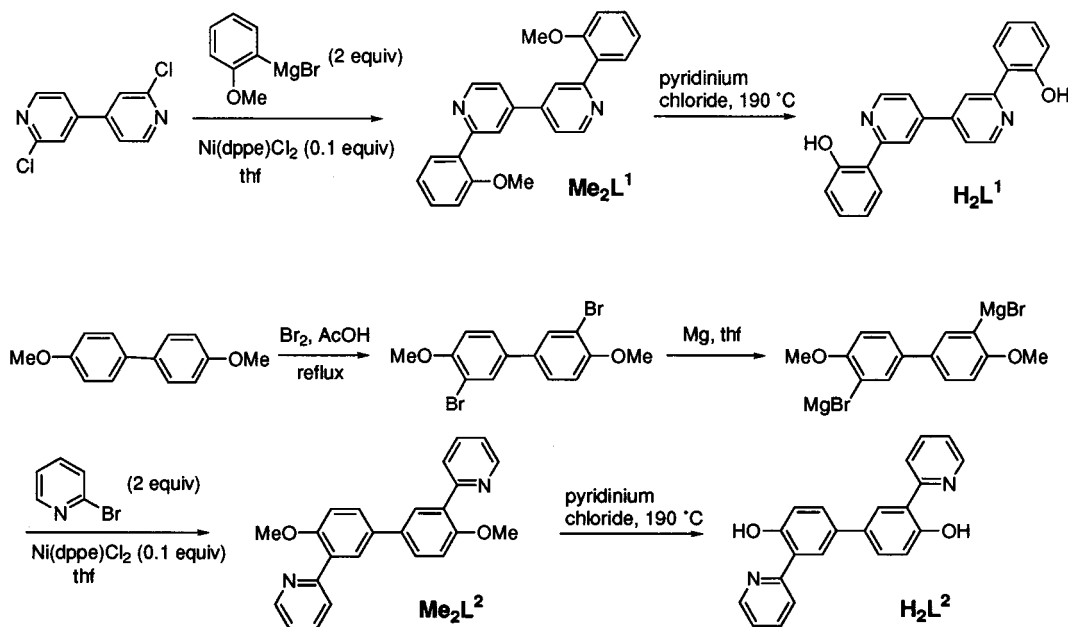
II in which the BL orbitals are much lower in energy (Figure 1b). The "reducible" BL stabilizes the reduced MV state [**II**]⁻ (ΔE between Mo(0)/Mo(I) couples is 765 mV, $K_c \approx 10^{13}$) because delocalization occurs by electron transfer through the BL LUMO (M⁻–L–M and M–L⁻–M are similar in energy). For the oxidized MV state [**II**]⁺ no such pathway is accessible: electron transfer via the LUMO would require charge separation (M⁺–L–M → M⁺–L⁻–M⁺), and the HOMO is too remote to permit delocalization by hole transfer, so the two Mo(I)/Mo(II) couples are essentially coincident.

Some of the most extensively studied MV complexes have been Ru(II)/Ru(III) complexes with N-heterocyclic ligands such as 4,4′-bipyridine and its analogues.[1,2,4] Many of these are actually not optimized to maximize delocalization in the MV state according to the principles above, because a MV state generated by oxidation cannot be effectively delocalized by a "reducible" BL (cf. the behavior of [**II**]⁺). In [(H₃N)₅Ru–(μ-4,4′-bipy)–Ru(NH₃)₅]⁵⁺, for example, K_c is only 24,[8] compared to 8.6×10^{12} for the reduced MV state [**II**]⁻ across the same bridging pathway.[6] Improving electronic communication in such Ru(II)/Ru(III) complexes requires BLs with higher-energy orbitals such that the HOMO can become involved in hole transfer, cf. [**I**]⁺, and in Ru(II)/Ru(III) MV complexes anionic BLs often result in stronger metal–metal coupling than do comparable neutral BLs for exactly this reason.[2b,4a] In particular, Haga et al.[9] and Vos et al.[10] have used protonation/deprotonation processes of triazole[9] or imidazole[10] groups in the bridging pathway to show that increasing the negative charge on the BL increases the metal–metal coupling.

We describe here a pair of isomeric dinuclear Ru(II) complexes in which the *only* difference between them is the nature of the bridging pathway: in one case we require high-energy orbitals (Figure 1a), and in the other case we require low-energy orbitals (Figure 1b). Following our work with the Mo complexes described above,[5–7] a suitable pair of BLs to compare would

be (deprotonated) 4,4′-biphenol for the former case and 4,4′-bipyridine for the latter; all other aspects of the complexes (charge, metal coordination environment, etc.) should be the same. Importantly, changing the BL linking the metals without changing the coordination environment of the metal center as a whole requires a compensating change elsewhere in the donor set. We have accordingly prepared complexes [(bipy)₂Ru(μ-L¹)Ru(bipy)₂][PF₆]₂ (**A**) and [(bipy)₂Ru(μ-L²)Ru(bipy)₂] [PF₆]₂ (**B**), in each of which two Ru(II) centers with an identical N₅O donor set are linked by 4,4′-bipyridyl and 4,4′-biphenolate bridges, respectively. There is a parallel between these and complexes **III** and **IV**, prepared by Collin et al., in which 4,4′-bipyridyl and 4,4′-biphenyldiyl bridges are compared.[2b]

We demonstrate that, following the above arguments, the 4,4′-biphenolate bridge affords a stronger metal–metal interaction than 4,4′-bipyridine despite a greater metal–metal separation, and that *p*-diphenolates of this type are accordingly promising candidates as effective bridging ligands in dinuclear Ru(II)/Ru(III) complexes.

Results and Discussion

The ligands H_2L^1 and H_2L^2 were prepared as shown in Scheme 1 and were converted to their dinuclear complexes **A** and **B** following standard methods. The analogous mononuclear complex **C** was reported earlier.[11] Electrochemical studies in CH_2Cl_2 clearly show the difference in how well the two types of bridging pathways facilitate metal–metal electronic coupling. In **A** a single, symmetric wave at +0.08 V vs Fc/Fc⁺ ($\Delta E_p =$ 90 mV) is ascribed to two coincident Ru(II)/Ru(III) couples [cf. +0.03 V vs Fc/Fc⁺ for the Ru(II)/Ru(III) couple of **C**].[11] The fact that the two processes cannot be separated is indicative of a weak electronic interaction, as commonly occurs for successive Ru(II)/Ru(III) couples across 4,4′-bipyridyl bridges.[1a,8] In contrast, **B** shows two distinct reversible one-electron processes at −0.09 and +0.06 V vs Fc/Fc⁺ ($\Delta E_p = 60$–70 mV), whose separation of 150 mV corresponds to $K_c \approx 350$ for the mixed-valence state [**B**]⁺. Two additional irreversible oxidations
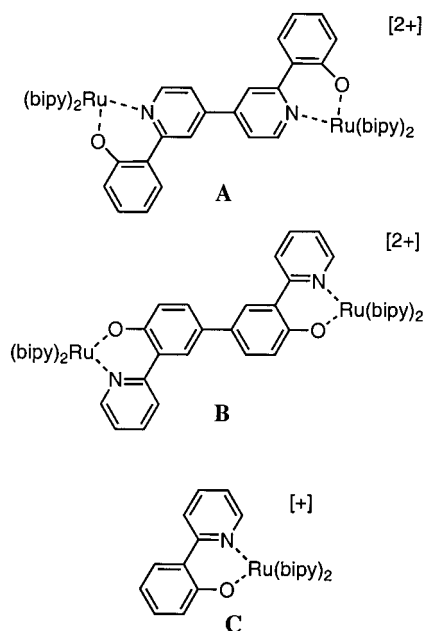
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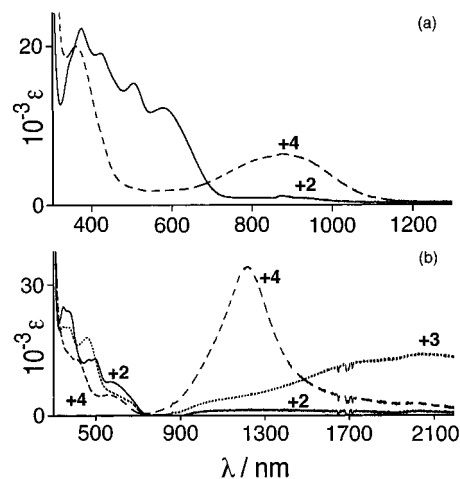
Figure 2. Results of spectroelectrochemical studies on (a) complex **A** and (b) complex **B** (CH_2Cl_2, 243 K).

Table 1. Electronic Spectra of the Complexes (CH_2Cl_2, 243 K)

complex	λ_{max}, nm ($10^{-3} \epsilon$, M^{-1} cm^{-1})
A	244 (67), 293 (87), 376 (22), 426 (19), 506 (15), 581 (11)
[A]$^{2+}$	245 (65), 283 (71), 361 (19), 870 (5.6)
B	246 (53), 291 (104), 346 (25), 376 (24), 467 (13), 497 (13), 572 (7.9)
[B]$^{+}$	246 (50), 291 (92), 345 (21), 372 (21), 457 (18), 670 (sh), 2000 (14)
[B]$^{2+}$	247 (50), 290 (92), 412 (13), 562 (4.5), 1218 (34)
C	246 (45), 294 (62), 342 (sh), 375 (15), 495 (7.6), 574 (sh)
[C]$^{+}$	246 (44), 295 (40), 860 (3.6)

at more positive potential (+0.76 and +1.02 V vs Fc/Fc$^+$) are assigned to oxidation of the central 4,4′-biphenolate unit to give a quinone;[12] the fact that these processes do not occur in the isomeric complex **A** confirms the assignment. This behavior contrasts with that recently described by Vos et al. for complex **V**, where the ligand-centered oxidations come before the metal-centered ones.[13] For both **A** and **B** poorly resolved and irreversible ligand-centered reductions occur at high negative potentials.

The results of spectroelectrochemical studies (CH_2Cl_2, 243 K) are in Figure 2 and Table 1. On oxidation of the mononuclear model complex **C** from the Ru(II) to the Ru(III) state, the area of absorbance between 450 and 650 nm [due to Ru(II) → bipy(π^*) or Ru(II) → pyridyl(π^*) MLCT transitions][11] substantially diminshes in intensity, and a new phenolate → Ru(III) LMCT transition appears at 860 nm ($\epsilon = 3600$ M^{-1} cm^{-1}) (Table 1). The behavior of complex **A** is strikingly similar to this (Figure 2a). In the Ru(II)/Ru(II) state there are several MLCT processes of which the lowest is at 602 nm. On oxidation to [A]$^{2+}$ [Ru(III)/Ru(III) state] these collapse and are replaced by a phenolate → Ru(III) LMCT at 863 nm ($\epsilon = 5600$ M^{-1} cm^{-1}). This is at a wavelength essentially identical to that of the analogous transition in complex [C]$^+$ but of greater intensity, consistent with the presence of two localized LMCT processes. Importantly, at no point during the oxidation did we detect any absorbance appearing in the near-IR region. Although we would expect some of the MV Ru(II)/Ru(III) complex [A]$^+$ to be present in the mixture when the applied potential was ca. +0.08 V (cf. the voltammetric results), for this weakly coupled system we assume that the IVCT transition is of high energy and low intensity—typical of other Ru(II)/Ru(III) complexes with 4,4′-bipy type bridges[1a,g]—and therefore obscured by the phenolate → Ru(III) LMCT process. For example, in the comparable MV complex [{Cl(bipy)$_2$Ru}$_2$(μ-4,4′-bipy)]$^{3+}$ (in which the phenolates of [A]$^+$ are replaced by chloride ligands) the IVCT transition is in the 900−1100 nm range (depending on solvent) with $\epsilon \approx 100$ M^{-1} cm^{-1};[14] such a weak transition would be swamped by the much stronger phenolate → Ru(III) LMCT of [A]$^+$.

Complex **B** behaves quite differently (Figure 2b). The first oxidation, to generate the Ru(II)/Ru(III) state [B]$^+$, results in the appearance of a broad, intense IVCT transition at about 2000 nm ($\epsilon = 14\,000$ M^{-1} cm^{-1}). Some fine structure is apparent on this, with shoulders at ca. 1700 and 1050 nm. For Ru(II)/Ru(III) MV complexes up to three components are expected for the IVCT transition when the geometry is not a perfect octahedron, because of the nondegeneracy of the three d(π) orbitals on the Ru(II) donor, and the separation of ca. 900 cm^{-1} between the two lower-energy features is consistent with this.[15] Nevertheless it is usual to ignore this and to treat the IVCT as a single transition.[1,15b] The shoulder at ca. 1050 nm is likely to be the phenolate → Ru(III) LMCT associated with the oxidized terminus.

From the parameters of the IVCT peak, and the calculated Ru···Ru separation of 13 Å, we estimate the electronic coupling V_{ab} to be 830 cm^{-1}.[16] This is considerably larger than the value of 390 cm^{-1} in [(H$_3$N)$_5$Ru−(μ-4,4′-bipy)−Ru(NH$_3$)$_5$]$^{5+}$[8] and comparable to the value of ca. 1000 cm^{-1} observed by Collin et al. in complex **III** across a 4,4′-biphenyldiyl bridge.[2b] This V_{ab} value, together with the value of K_c derived from the electrochemistry, is consistent with Robin-Day class II behavior; the width of the IVCT transition also agrees with this.[17]

On further oxidation to the Ru(III)/Ru(III) state [B]$^{2+}$, the IVCT transition disappears and is replaced by an intense

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(16) Calculated from the Hush formula: $V_{ab} = \{[2.05 \times 10^{-2} (\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2}]/R\}$, where ϵ_{max}, $\bar{\nu}_{max}$, and $\Delta\bar{\nu}_{1/2}$ are the molar extinction coefficient, the absorption maximum in wavenumbers, and the bandwidth at half-maximum height in wavenumbers, respectively; and R is the metal−metal distance in angstroms. Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

transition at 1208 nm ($\epsilon = 34\,000$ M^{-1} cm^{-1}), which, by analogy with the spectra of $[A]^{2+}$ and $[C]^{+}$, has phenolate → Ru(III) LMCT character.[18] The low energy of this transition compared to that of $[A]^{2+}$ is due to the high energy of the HOMO centered on the bis-phenolate bridging fragment; and its high intensity indicates how effectively the bridging bis-phenolate fragment acts as an electron donor to the Ru(III) centers. These are the exact features which are necessary to optimize delocalization in the MV state by hole transfer via the bridging-ligand HOMO.

In conclusion, it is clear from comparison of the properties of **A** and **B** how matching the nature of the bridging ligand to the redox characterstics of the metal fragments can maximize the metal−metal interaction and permit long-distance optical electron transfer in MV states. Bis-phenolate bridging ligands, which have received very little attention for the preparation of dinuclear Ru(II)/Ru(III) complexes,[13] are clearly promising candidates for further study in this respect.

Experimental Section

Electrochemical and spectroelectrochemical experiments were carried out as described previously.[19] During the spectroelectrochemical experiments, all redox processes were checked for chemical reversibility by reversing the potential change and regenerating the spectrum of the starting material.

The [Ni(dppe)Cl₂]-catalyzed cross couplings used to prepare Me_2L^1 [from 3,3′-dichloro-4,4′-bipyridine[20] and 2-bromoanisole (2.3 equiv)] and Me_2L^2 [from 2-bromopyridine and 3,3′-dibromo-4,4′-dimethoxy-biphenyl (0.5 equiv)] followed a general published method.[11,21] Demethylation of these to give H_2L^1 and H_2L^2 using molten pyridinium

chloride at 190 °C also followed a published method.[22] Full details together with spectroscopic data are in the Supporting Information.

Complexes **A** and **B** were prepared in an identical manner. To a solution of [Ru(bipy)₂Cl₂]·2H₂O (0.192 g, 0.37 mmol) in ethanol (20 cm³) was added a solution of AgNO₃ (0.126 g, 0.74 mmol) in water (10 cm³). After reflux for 0.5 h, the AgCl was filtered off, to the deep red filtrate were added H_2L^1 or H_2L^2 (0.060 g, 0.17 mmol) and Et₃N (several drops), and the mixture was heated to reflux for 4 h. Concentration in vacuo and addition of aqueous NH₄PF₆ precipitated the product, which was filtered off, dried, and purified by chromatography on silica using MeCN/water/saturated aqueous KNO₃ (20:2:1) as eluent (yields 60−70%). FABMS: m/z 1164 ($M^{+} - 2PF_6$), 1310 ($M^{+} - PF_6$) for both complexes. Found for **A**: C, 50.9; H, 3.1; N, 9.6. Found for **B**: C, 50.7; H, 2.9; N, 9.5. Required for both: C, 51.2; H, 3.2; N, 9.6.

Supporting Information Available: Preparation and characterization of ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Calculated from $\Delta\bar{\nu}_{1/2} = [2310(\bar{\nu}_{max})]^{1/2}$, which holds for class II MV states, but not class III complexes where the width $\Delta\bar{\nu}_{1/2}$ tends to be much less than this equation suggests. For $[B]^{+}$ this equation predicts $\Delta\bar{\nu}_{1/2} = 3400$ cm^{-1}, in reasonable agreement with the measured value of 4000 cm^{-1}. The fact that the measured width is slightly greater than predicted may be due in part to the presence of three closely spaced components in the IVCT transition (see ref 15).

(18) That this transition is about 10 times more intense than the analogous transition in the Ru(II)/Ru(III) state $[B]^{+}$ is surprising: in a class I or weakly interacting class II complex the spectra (apart from IVCT processes) should be approximately additive, such that the phenolate → Ru(III) LMCT transition is about twice as intense in the Ru(III)/Ru(III) state as in the Ru(II)/Ru(III) state. One possible exaplanation is that, on the second oxidation, a conformational change occurs in the bridging ligand from twisted to planar. The partial ligand-centered character of these redox processes would mean that the bridging ligand in the doubly oxidized complex has some quinonoidal character, resulting in an increase in the π-bond order between the two phenyl rings. See for example: Joulié, L. F.; Schatz, E.; Ward, M. D.; Weber, F.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1994**, 799.

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