

Molecular Design for Long-Range Electronic Communication between Metals

POLYNYNE AND ETHYNYLATED AROMATIC SYSTEMS AS MOLECULAR WIRES
IN BINUCLEAR RUTHENIUM β -DIKETONE COMPLEXES

By Yoshimasa Hoshino

Department of Chemistry, Faculty of Education, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

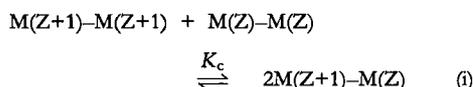
To construct molecular devices it is necessary to use mixed-valence metal complexes which have a large metal-metal separation distance and which exhibit strong coupling between the metals, so that errors which might arise from electrostatic interaction between the metal ions are prevented. Bridges, or spacers, are needed between two metal terminal sites to operate as effective molecular wires when one metal terminal site is in the excited state, and/or when both the terminal components are in the ground state. Binuclear ruthenium complexes, consisting of tris(β -diketonato)ruthenium(III) units, which are suitable as the terminal redox sites, can be used to evaluate how well the bridges function as molecular wires in the ground state. This is because their Ru(III)-Ru(II) and Ru(IV)-Ru(III) mixed-valence states are accessible for experimental use. In this article, a polyynene system and an ethynylated aromatic system are evaluated as molecular wires, using the binuclear (β -diketonato)ruthenium(III) complexes containing these systems as the bridges. In the Ru(IV)-Ru(III) mixed-valence state, the ruthenium complexes show relatively strong electronic interactions between the metal centres. This is interpreted by a superexchange (through-bond) hole transfer mechanism via the highest occupied molecular orbitals of the bridge. Molecular orbital calculations provide a guide to the molecular design of bridging ligands for long-range electronic coupling.

Mixed-valence binuclear complexes have been actively studied since 1969 when Creutz and Taube reported the fascinating mixed-valence ion, $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pz})\text{Ru}(\text{NH}_3)_5]^{3+}$ (pz = pyrazine), the so called 'Creutz-Taube ion' (1). Studies on mixed-valence complexes are closely related to the kinetics of electron transfer reactions, and provide valuable information on the degree of interaction between two metal sites. In such studies, three classes of symmetrical binuclear systems may be distinguished, depending on the degree of the electronic coupling between the two metal ions (2, 3).

In the Class I system, the electronic coupling is so weak that the mixed-valence complex exhibits only the properties of the isolated mononuclear complexes. The Class II system has electronic coupling to some extent, so the mixed-valence complex exhibits slightly perturbed mononuclear characteristics but also has obvious properties not associated with the isolated units. This system

remains 'valence trapped' or charge localised. In the Class III system, the coupling is so large that the properties of the isolated mononuclear complexes are absent and only new properties are discerned. This is the delocalised case.

We can estimate the extent of the metal-metal interactions by the stability of the binuclear complex formed in a 'comproportionation' (reverse of disproportionation) reaction, in which the oxidation numbers of the metals mix. The comproportionation reaction for the Class II system is:



where M represents the metal and Z the oxidation number. The comproportionation constant (equilibrium constant of Equation (i)), K_c , and the free energy change for the comproportionation, ΔG_c , are calculated from the difference in the reversible

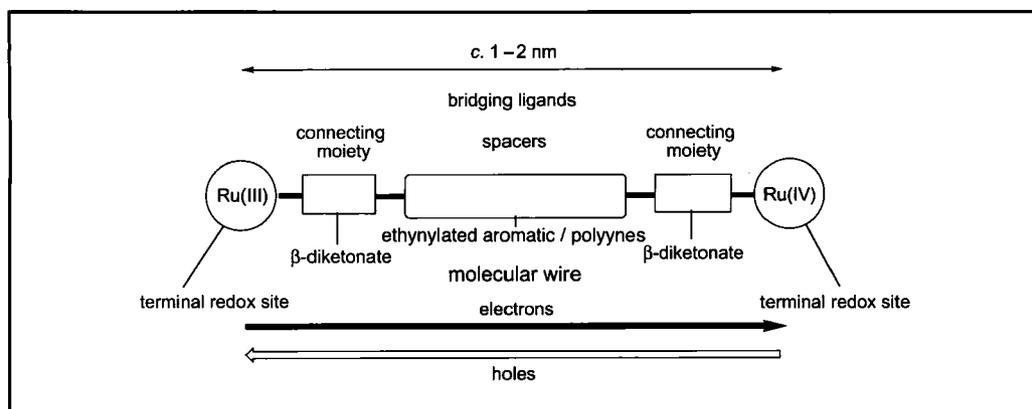
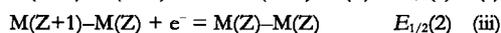
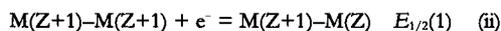


Fig. 1 Schematic diagram of the molecular wire system showing its structure; the ruthenium centres, which are terminal redox sites, are connected via the β -diketonate moieties with ethynylated aromatic/polyene groups as the spacers. In this system electrons move to the right and holes to the left

half-wave potentials between the two reduction potentials $\Delta E_{1/2} = (E_{1/2}(1) - E_{1/2}(2))$.



$$K_c = \exp(\Delta E_{1/2} F / RT) \quad (\text{iv})$$

$$\Delta G_c = -\Delta E_{1/2} F \quad (\text{v})$$

The free energy change of the comproportionation, ΔG_c , is expressed by the Equation:

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \quad (\text{vi})$$

where ΔG_s is an entropy factor, ΔG_e is an electrostatic factor arising from the repulsion of the two similarly charged metal centres, ΔG_i is an inductive factor dealing with the competitive coordination by metal ions for the bridging ligand, and ΔG_r is the free energy of resonance exchange which represents the actual metal-metal coupling (3, 4).

For a strongly coupled system with a large metal-metal distance ($d(M-M) > \sim 1.5$ nm), the resonance exchange term (ΔG_r) dominates ΔG_c , because the electrostatic factor (ΔG_e) exponentially decreases with the increasing charge separation, the entropy factor (ΔG_s) has a constant value of $-RT \ln 4$, and the contribution of the inductive factor (ΔG_i) is generally small. In such a system the degree of the metal-metal coupling can be estimated by the K_c value.

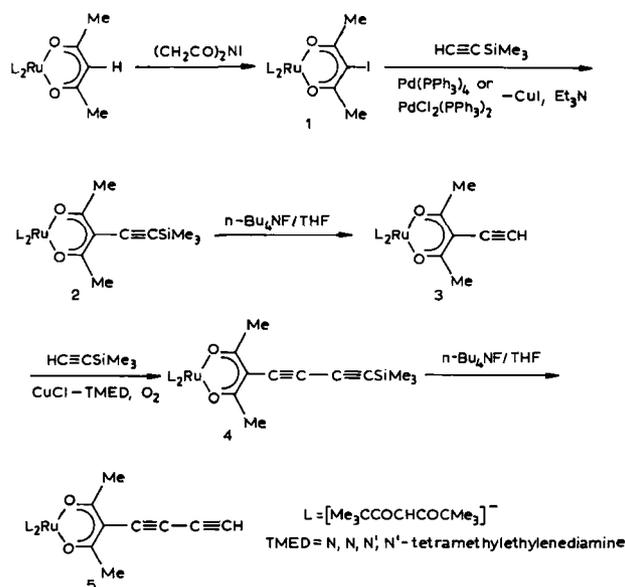
Thus the value of the comproportionation constant K_c is important for the design of bridging ligands. Studying mixed-valence systems with large

metal-metal distances which show strong metal-metal coupling is needed to gather information about electron transfer in inorganic and biological systems and to aid construction of molecular devices. In constructing molecular devices the through-space distance between the donor and acceptor should be big (not the through-bond distance) in order to prevent errors arising from any electrostatic interaction. Mixed-valence ruthenium complexes have been reported, which despite having a metal-metal distance $d(M-M) > 1.0$ nm, have relatively strong metal-metal coupling, that is, large comproportionation constants ($K_c > 10^3$) (4b, 5). However, to the author's knowledge, large K_c values have never been reported for any binuclear complex (not an organometallic compound) with a metal-metal distance $d(M-M) > 2.0$ nm.

One of the aims of our research, therefore, is to produce a guide that can be used in the design of molecular bridging ligands which will be able to achieve good metal-to-metal communications over a long metal-metal distance.

Spacers between the Metal Terminal Sites

The polyene system is one of the most effective spacers for potential long-range electronic communication between two redox centres. In fact, butadiyne (C_4 spacer)- and octatetrayne (C_8 spacer)-bridged diiron organometallic compounds, where the polyynes directly connect to the metal



Scheme 1

Introducing an ethynyl group into a β -diketonate chelate and oxidative coupling of ethynyl compounds showing how ethynyl links can be used for elongation for wires

centre, exhibit quite large K_c values: 1.60×10^{12} for the C_4 spacer and 2×10^7 for the C_8 spacer (6). Furthermore, the C_{12} and C_{16} μ -polyynediyl dirhenium complexes exhibit two one-electron oxidation steps in their cyclic voltammograms: for the C_{12} spacer $\Delta E_{1/2}$ is 0.19 V, and for the C_{16} spacer $\Delta E_{1/2}$ is 0.09 V (7). However, ethynyl and butadiynyl bridges actively promote long-range electronic coupling between remote cationic units when illuminated with visible light (8).

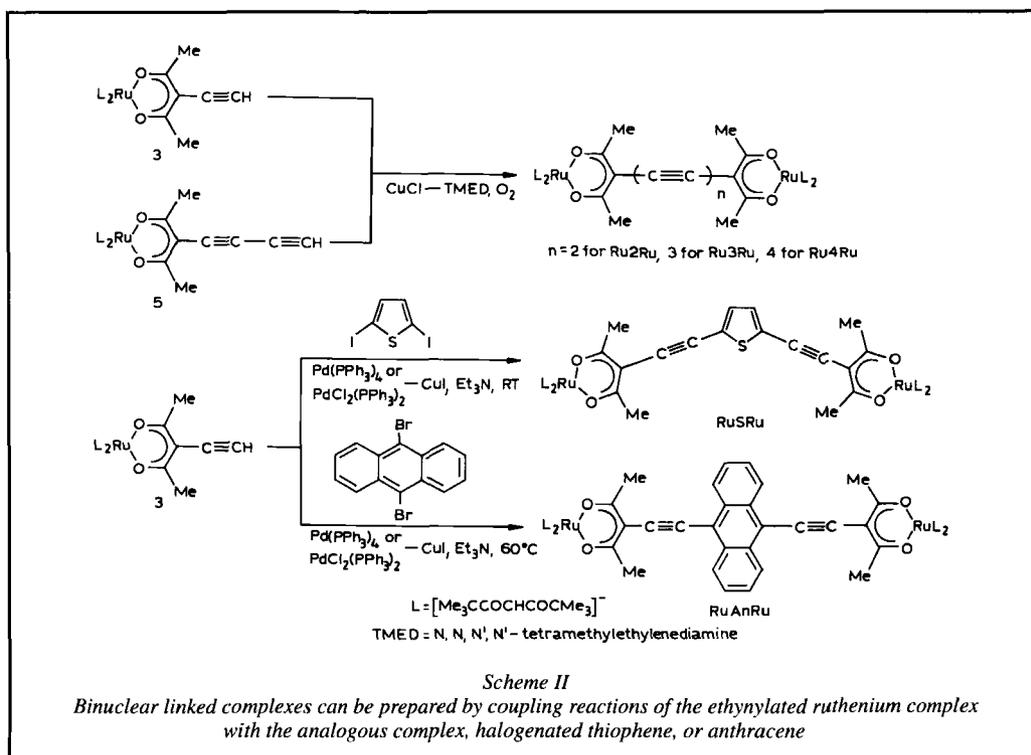
It has not been proved that the polyyne system in the ground state of mixed-valence systems, where polyynes indirectly connect to the metal centre, operate as molecular wires between the redox metal sites; the K_c values of the diruthenium complex bridged by bis(4-pyridyl)acetylene (9) and of the ruthenium and osmium polypyridyl complexes linked by bridging polyynes (10) are very small.

The functioning of the polyyne system as molecular wires in the ground state of mixed-valence complexes depends on the characteristics of the connecting moiety between the bridges and the metal centres, see Figure 1. To evaluate the

polyyne system β -diketonate was chosen as the connecting moiety because the β -diketonate chelate has aromaticity and a $p\pi$ conjugated system, which can interact with the $d\pi$ orbitals of a metal centre. The distance between a metal and a terminal carbon of the polyyne bridge (at the γ -position of a β -diketonate ring) is shorter than any involving pyridine rings used previously (except at carbons adjacent to ligating nitrogen atoms). Thus, we chose tris(β -diketonato)ruthenium(III) units as the redox sites. These can be electrochemically oxidised and reduced to give ruthenium(IV) and ruthenium(II) species (11). Therefore, the degree of interactions between two redox sites bridged by a polyyne system and an ethynylated aromatic system in two kinds of mixed-valence states, Ru(IV)-Ru(III) and Ru(III)-Ru(II), can be found.

Syntheses of Binuclear Ruthenium Complexes

Because of the quasi-aromatic reactivity of the γ -methyne of a β -diketonate chelate ring, it should be possible to introduce an alkyne group at the γ -position. No such synthesis has yet been described,



although a wide variety of γ -substitution reactions are known, for example, halogenation, nitration and acetylation (12). We have successfully introduced an ethynyl group into this γ -position, using Sonogashira reaction-type palladium catalysts (13). Ethynyl links can be elongated by oxidative coupling (14), see Scheme I, (15). Binuclear complexes, including ethynylated thiophene-bridged (S) and anthracene-bridged (An) complexes, can be prepared by similar coupling reactions, see Scheme II, (16). These complexes have been characterised by 1H NMR and IR spectroscopies and by mass spectrometry (13, 16). The 1H NMR spectra of these binuclear complexes show paramagnetic shift because of an unpaired electron in the Ru^{III} metal centre, and do not contradict the spectra derived from the expected structure.

The IR spectra show the characteristic $C\equiv C$ stretching vibrations in the region from 2100 to 2200 cm^{-1} . In their FAB mass spectra, the observed parent peaks correspond to the molecular weight of these binuclear complexes. Preparing

single crystals of these complexes has often been attempted, but insufficient crystals for X-ray structure analysis have been obtained.

Electrochemical Properties

A typical cyclic voltammogram of a binuclear ruthenium complex (**RuAnRu**) is shown in Figure 2. The two pairs of peaks on the positive side of the voltammogram correspond to two consecutive, Nernstian, one-electron oxidation steps (one pair of peaks (A and D) corresponds to the $Ru^{IV}-Ru^{III}/Ru^{III}-Ru^{III}$ couple, and the other pair of peaks (B and C) correspond to the $Ru^{IV}-Ru^{IV}/Ru^{IV}-Ru^{III}$ couple). The pair of peaks (E and F) on the negative side can be assigned to two overlapping one-electron reduction processes. The reduction steps of **RuAnRu** and **RuSRu** can be assigned to the reduction of the metal centres, while the oxidation steps correspond to metal-based oxidation and not to ligand-based oxidation (16). Values for the reversible half-wave potentials ($E_{1/2}$), K_c and for the estimated metal-metal distances in the complexes are given in Table I (13, 15, 16).

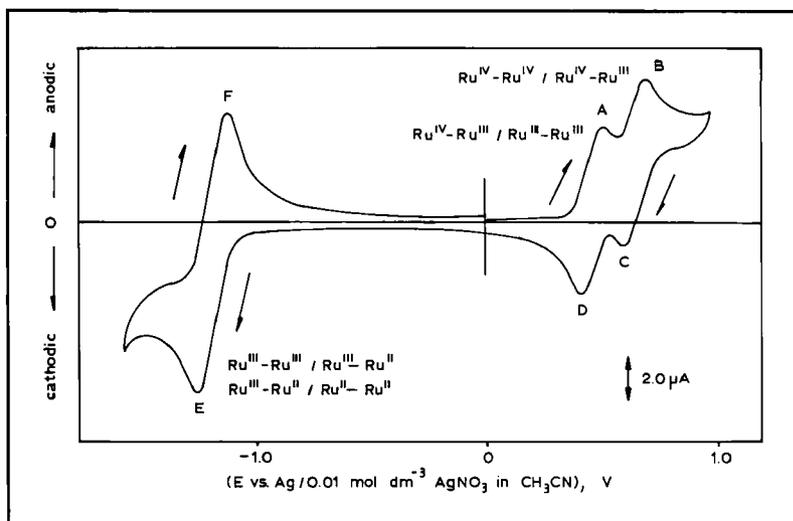


Fig. 2 The cyclic voltammogram for **RuAnRu** in 0.1 mol dm^{-3} of $(\text{C}_4\text{H}_9)_4\text{NBF}_4\text{-CH}_2\text{Cl}_2$ on a platinum disk electrode at 25°C . The sweep rate was 0.1 V s^{-1}

Five oxidation states, including the original oxidation state of these binuclear complexes, are electrochemically accessible as expected: Ru(II)-Ru(II), Ru(III)-Ru(II), Ru(III)-Ru(III), Ru(IV)-Ru(III) and Ru(IV)-Ru(IV). The bridging ligands containing the polyyne and the ethynylated aromatic groups can now be evaluated as molecular wires in the two mixed-valence states, Ru(IV)-Ru(III) and Ru(III)-Ru(II).

K_c Values for the (III, II) and (IV, III) States

The $K_c(\text{III}, \text{II})$ values are significantly smaller than the $K_c(\text{IV}, \text{III})$ values; $K_c(\text{III}, \text{II})$ values of **Ru3Ru** and **Ru4Ru** in particular are close to the

statistical limit ($K_c = 4$). This indicates that the free energy change of the comproportionation, $\Delta G_c(\text{III}, \text{II})$, which is the stabilisation of the Ru(III)-Ru(II) mixed-valence system, is small, and also that the electron resonance exchange term, $\Delta G_r(\text{III}, \text{II})$ is only a minor factor contributing to $\Delta G_c(\text{III}, \text{II})$, see Equation (vi). On the other hand, $\Delta G_r(\text{IV}, \text{III})$ is a major factor contributing to the $\Delta G_c(\text{IV}, \text{III})$ of the Ru(IV)-Ru(III) system. Therefore the degree of the electronic coupling between the metal centres in the Ru(IV)-Ru(III) state is much larger than that in the Ru(III)-Ru(II) state.

In the present systems, see Figure 3, it is energetically favourable for a hole to move from the

Complex	$\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$		$K_c(\text{IV}, \text{III})$	$\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$		$K_c(\text{III}, \text{II})$	$d(\text{M-M})$, nm
	$E_{1/2}$, V	$\Delta E_{1/2}$, mV		$E_{1/2}$, V	$\Delta E_{1/2}$, mV		
RuAnRu	0.280, 0.463	183	1200	-1.344, -1.424	80	22	1.71
RuSRu	0.383, 0.558	175	900	-1.334, -1.414	80	22	1.67
Ru2Ru	0.396, 0.621	225	6360	-1.361, -1.472	111	75	1.31
Ru3Ru	0.465, 0.589	124	125	-1.319, -1.372	53	8	1.56
Ru4Ru	0.516, 0.602	86	28	-1.260, -1.315	55	8	1.82

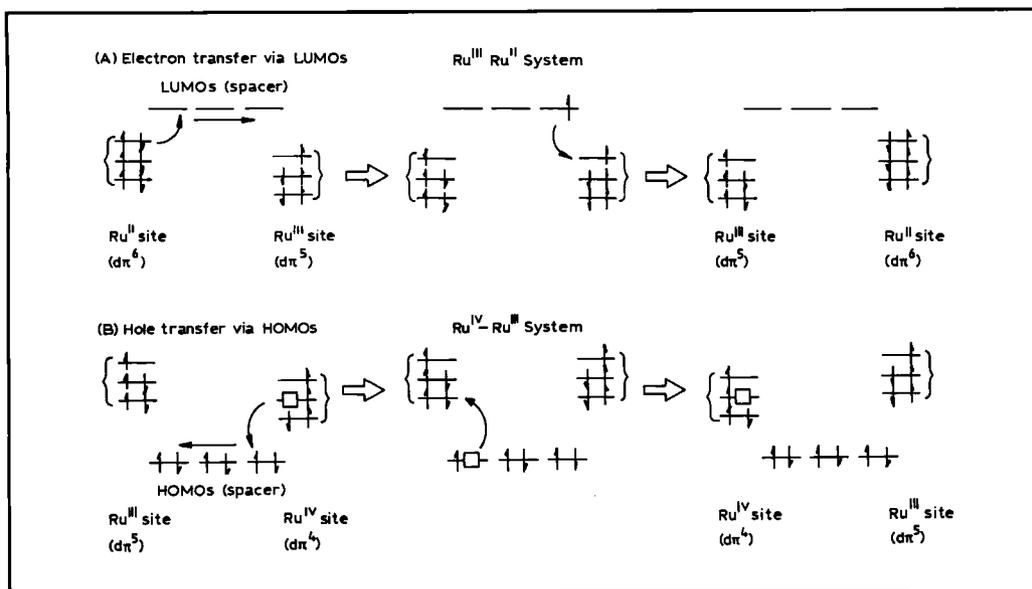


Fig. 3 Superexchange mechanisms for the intramolecular transfer of electrons and holes. Electron transfer is shown from the $d\pi^6$ Ru(II) site via the lowest unoccupied molecular orbitals (LUMOs) of the bridge to the $d\pi^5$ Ru(III) site. Hole transfer is shown from the $d\pi^4$ Ru(IV) site via the highest occupied molecular orbitals (HOMOs) of the bridge to the $d\pi^5$ Ru(III) site

$d\pi$ orbital of the ruthenium(IV) site to one of the ruthenium(III) sites via the highest occupied molecular orbitals (HOMOs) of the bridge in the ground state of the Ru(IV)-Ru(III). On the other hand, in the Ru(III)-Ru(II) system, electron transfer from the ruthenium(II) site to the ruthenium(III) site via the lowest unoccupied molecular orbitals (LUMOs) of the bridge is favourable. Such a hole- or electron-transfer mechanism is called a 'through-bond' mechanism and often called the 'superexchange' mechanism (17).

The large difference between the $\Delta G_r(\text{IV}, \text{III})$ and $\Delta G_r(\text{III}, \text{II})$ indicates the large difference between the degree of electronic coupling for the hole transfer and for the electron transfer. This large difference between hole and electron transfer can be interpreted by the difference in character of HOMOs and LUMOs of the bridging ligands, as mentioned below.

Recently, we have prepared the following:

- a new metal coordination polymer of ruthenium(III) β -diketone units linked by a butadiyne bridge;
- a mononuclear complex $[\text{Ru}^{\text{III}}(\text{mEma})_3]$ ($\text{mEma}^- = 3\text{-ethynyl-2,4-pentanedionate ion}$) as the

starting material for the polymerisation (18) and (c) their electrochemically reduced products, $\text{poly-}[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ and $[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$.

To our surprise, spectroelectrochemical measurements showed that the visible spectra for the $\text{poly-}[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ (new band at 499 nm) and the $[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ (new band at 497 nm) are approximately the same. The new band of $[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ is assigned to metal-to-ligand charge transfer (MLCT) – a transition from the metal $d\pi$ level to the ligand $\text{mEma}^- \pi^*$ orbitals, while the new band of $\text{poly-}[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ comes from the combination of two of the MLCT bands; one band corresponds to transitions from the $d\pi$ levels to the terminal $\text{mEma}^- \pi^*$ orbitals and the other is transitions from the $d\pi$ levels to the bridging ligand, the $\text{tahdy}^{2-} \pi^*$ orbitals ($\text{tahdy}^{2-} = 1,1,6,6\text{-tetraacetyl-2,4-hexadiynate dianion}$). In spite of the combination, the shape of the absorption bands of $\text{poly-}[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$ are consistent with those of $[\text{Ru}^{\text{II}}(\text{mEma})_3]^-$: both bands have a shoulder near 460 nm. With this observation, it is possible to predict that the energy levels of the $\text{tahdy}^{2-} \pi^*$ orbitals are approximately equal to those of the $\text{mEma}^- \pi^*$ orbitals.

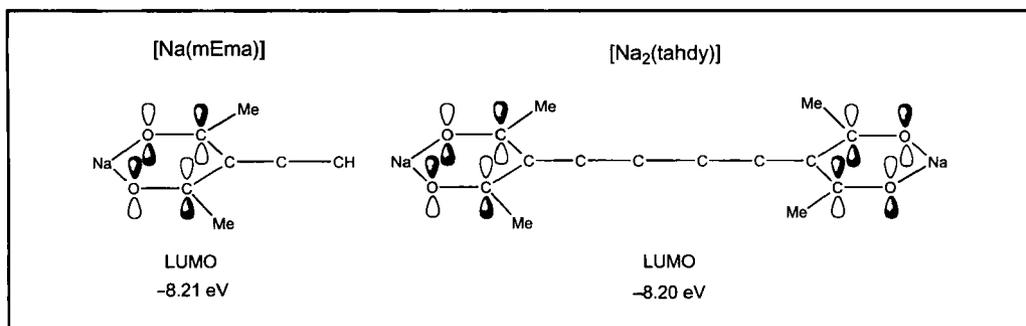


Fig. 4 Schematic of the lowest unoccupied molecular orbitals (LUMOs) of $[\text{Na}(\text{mEma})]$ and $[\text{Na}_2(\text{tahdy})]$

To confirm this prediction, extended Hückel molecular orbital (EHMO) calculations were carried out for $[\text{Na}(\text{mEma})]$ and $[\text{Na}_2(\text{tahdy})]$ as model compounds for $[\text{Ru}(\text{mEma})_3]$ and poly- $[\text{Ru}(\text{mEma})_3]$, respectively (18). The calculations show that the LUMO energy level of $[\text{Na}_2(\text{tahdy})]$ is approximately equal to that of $[\text{Na}(\text{mEma})]$. Both of the LUMOs have a node on the 3-position carbon atom of the β -diketone ring, see Figure 4, so that there is no wavefunction on the ethynyl carbons of $[\text{Na}(\text{mEma})]$ or on the butadiynyl carbons of $[\text{Na}_2(\text{tahdy})]$. Therefore, the LUMO of $[\text{Na}_2(\text{tahdy})]$ is essentially the same as that of $[\text{Na}(\text{mEma})]$. On the other hand, the π -conjugated system in the second highest occupied molecular orbital (SHOMO) of $[\text{Na}_2(\text{tahdy})]$ is extended through the entire bridging ligand (18).

Consequently, the atomic orbitals of the ethynyl bridge do not contribute to the LUMO of the tahdy^{2-} bridging ligand. The LUMOs of the other analogous tetraketone bridging ligands in this study should have a node, so the superexchange would not operate for electron transfer via LUMOs of the bridge in the ground state of the Ru(III)-Ru(II) systems.

Metal-to-Metal Communication in the Ru(IV)-Ru(III) State

According to the Marcus-Hush theory (19) (which links the rate of electron transfer of electrons from one molecule to another, or from part of a molecule to another, in terms of structural changes in the molecule. For a large molecular rearrangement the rate of electron transfer will be slow, while for small molecular rearrangements the

rate will be fast) and superexchange theory (8c, 20):

$$-\Delta G_{\text{r}} = 2H_{\text{ab}}^2/\lambda \quad (\text{vii})$$

$$H_{\text{ab}} = (H_{\text{ab}})_0 \exp[-\beta R/2] \quad (\text{viii})$$

$$H_{\text{ab}} = c_{\alpha} c_{\beta} / \delta E \quad (\text{ix})$$

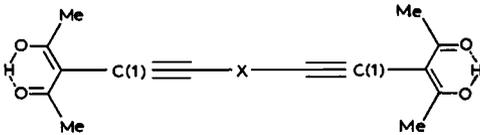
Here, ΔG_{r} depends on the electronic coupling matrix element, H_{ab} , where $(H_{\text{ab}})_0$ is the matrix element when donor and acceptor orbitals are in contact, and λ is the reorganisation parameter; β reflects the efficacy of the medium during donor-acceptor coupling and R is the length of the bridge; c_{α} is the atomic orbital coefficient for the coupling between the donor and the bridge, and c_{β} is the atomic orbital coefficient for the coupling between bridge and acceptor; δE represents the energy gap between the appropriate orbitals on the donor(acceptor) and the bridge.

For the homologous series of Ru_nRu ($n =$ the number of ethynyl groups = 2, 3, and 4), the $K_{\text{c}}(\text{IV}, \text{III})$ values decrease exponentially with the increasing number of ethynyl bridges; in particular, the $K_{\text{c}}(\text{IV}, \text{III})$ value for Ru_4Ru is close to the corresponding $K_{\text{c}}(\text{III}, \text{II})$ value (15). This result is in accord with the distance, R , dependence of H_{ab} (Equation (viii)) (21). Thus, strong electronic coupling is not expected for the Ru_nRu system when $n > 4$ with polyyne as the bridge and the β -diketone chelate as the connecting moiety. Therefore, an increase in the $K_{\text{c}}(\text{IV}, \text{III})$ value with decreasing δE was planned by inserting another conjugated moiety with electron-donor ability, that is thiophene and anthracene units, into the ethynyl bridges (16).

In fact, although the $d(\text{M-M})$ of Ru_nRu (1.71 nm) and RuSRu (1.67 nm) are both longer than

Table II

Values of the SHOMO Energy (E_h), the Sum of Squared Extended Hückel MO Coefficients at the Terminal Carbons (C(1)) of the Triple Bond in Tetraketones, ΣC_1^2 , and Square Roots of the Natural Logarithms of the Comproportionation Constants (K_c) of Various Binuclear Ruthenium Complexes



H_2BL (X)*	E_h , eV	ΣC_1^2	Complex	$(\ln K_c(IV, III))^{1/2}$
H_2An ($C_{14}H_6$)	-10.60	0.196	RuAnRu	2.67
H_2S (C_4H_2S)	-10.83	0.185	RuSRu	2.61
H_22 (none)	-11.22	0.198	Ru2Ru	2.96
H_23 (C_2)	-11.22	0.158	Ru3Ru	2.20
H_24 (C_4)	-11.22	0.138	Ru4Ru	1.83

*BL denotes bridging ligand

that of **Ru3Ru** (1.56 nm), the $K_c(IV, III)$ values for **RuSRu** and **RuAnRu** are larger than that for **Ru3Ru** by a factor of about 10. This indicates that metal-to-metal communication in the Ru(IV)-Ru(III) mixed-valence state, that is, the electronic coupling, is amplified by inserting other conjugated moieties with electron-donor ability into the two ethynyl groups. This amplification seems to be caused by decreased δE , due to the presence of the electron-donor groups in the bridge. This can be confirmed by EHMO calculations for a series of tetraketones, H_2BL , whose dianions are net bridging ligands (BL). The SHOMO energies (E_h), which correspond to the $p\pi$ HOMO energies of

the bridging ligands in the complexes, are given in Table II (22). The π -conjugated system in the SHOMO of H_2S is extended through the entire bridging ligand, see Figure 5. The SHOMO energy levels of H_2An and H_2S are higher than that of H_23 . From these calculations we can foresee that the energy gap between the $d\pi$ orbitals of the metal centres and the $p\pi$ HOMO of the bridging ligands in **RuAnRu** and **RuSRu** becomes smaller compared with that in **Ru3Ru**.

On the other hand, the SHOMO energies (E_h) of the H_2n system, see Table II, are in good agreement with each other ($= -11.22$ eV) and are constant. This result predicts that the energy gap

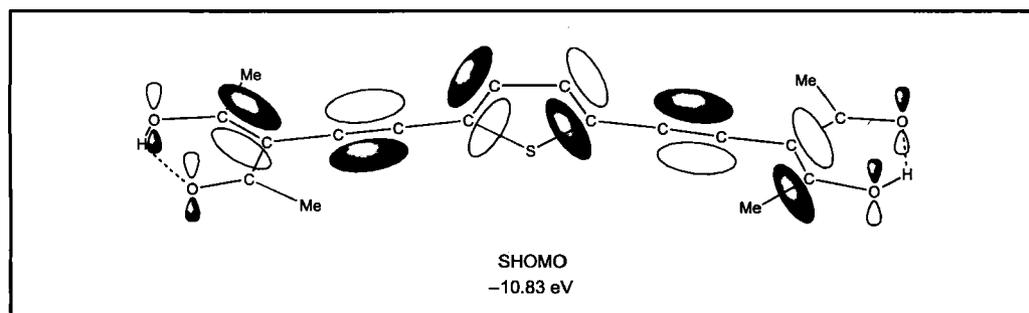


Fig. 5 Schematic of the second highest occupied molecular orbital (SHOMO) of H_2S . The π -conjugated system in the SHOMO of H_2S is extended through the entire bridging ligand

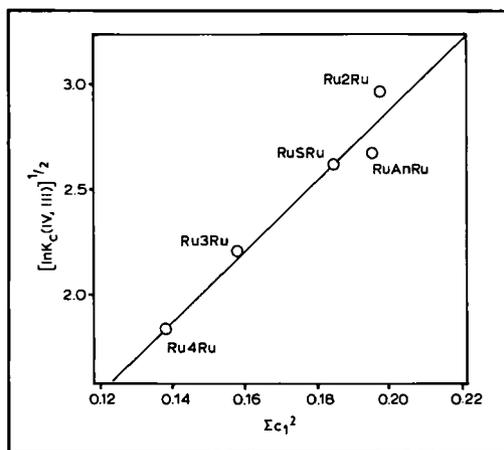


Fig. 6 The linear relationship between the square root of $\ln K_c(\text{IV, III})$ values, for various binuclear ruthenium complexes, and the sum of the squared extended Hückel MO coefficients Σc_1^2 in SHOMO at the terminal carbons (C(1)) of the triple bond in tetraketones, is clearly seen. This relationship can be used as a guide for designing molecular wires based on this system

(δE) between the $d\pi$ orbitals of the metal centres and the $p\pi$ HOMO of the bridging ligands in **RunRu** is almost constant. Therefore the decrease in the $K_c(\text{IV, III})$ values in the **RunRu** system (from 6360 to 28) as the number of ethynyl groups (n) increases (2 to 4) cannot be interpreted by changes in δE . According to the superexchange mechanism (Equation (ix)), when the δE values for a series of binuclear complexes are almost constant, H_{ab} is then directly proportional to the product of e_α and e_β (coupling strength terms). Therefore, it is expected that the square root of $\ln K_c(\text{IV, III})$ bears a linear relationship to the product of e_α and e_β (Equations (iv), (v), (vii) and (ix)):

$$\{\ln K_c(\text{IV, III})\}^{1/2} \propto e_\alpha e_\beta \quad (\text{x})$$

Here, e_α (or e_β), which describes the coupling between the donor (or acceptor) and the bridge, can be considered as the orbital coefficient at the terminal atom of the bridge, because the magnitude of the coupling firstly depends on the probability density of finding the electron at the terminal atom.

Figure 6 shows the linear relationship between values of square roots of $\ln K_c(\text{IV, III})$ and Σc_1^2 , the sum of the squared extended Hückel MO coefficients, see Table II, for SHOMO at the terminal

carbons (C(1)) of the triple bond in the tetraketones. This relationship can thus be used as a guide for the molecular design of mixed-valence (tetraketonato)diruthenium complexes with long-range hole transfer.

Conclusions

The evaluation of a polyyne system and an ethynylated aromatic system as molecular wires using binuclear ruthenium β -diketonate complexes has been discussed. Binuclear species based on tris(β -diketonato)ruthenium(III) units can be used to evaluate bridges as molecular wires as their Ru(III)-Ru(II) and Ru(IV)-Ru(III) states are experimentally accessible within the potential window of common supporting electrolyte solutions. The binuclear complexes are also useful for investigating the superexchange mechanism, as the absence of wavefunctions on the bridge in the LUMOs of the bridging ligands simplifies the mechanism into a single pathway – a hole transfer process. In fact, the mixed-valent properties of dimeric ruthenium(III) complexes containing sulfur-substituted bridging β -diketonate rings are currently under investigation by Professor Shimizu's research group (23).

Molecular orbital calculations performed on bridging ligands containing a connecting moiety between a bridge and a metal centre provide a linear relationship between the square root of $\ln K_c$, substituted for the electronic coupling, and the sum of the squared extended Hückel MO coefficients, Σe_1^2 , substituted for the product of atomic orbital coefficients ($e_\alpha e_\beta$). Using this relationship, mixed-valence complexes with even longer metal-metal distances (> 2.0 nm), with strong electronic coupling (large K_c values) can be designed.

Acknowledgements

It is a pleasure to express my appreciation to Associate Professor Yasuhiko Yukawa, Niigata University, Japan, for reading and commenting on the manuscript.

References

- 1 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988
- 2 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247
- 3 C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1

- 4 (a) J. E. Sutton and H. Taube, *Inorg. Chem.*, 1981, 20, 3125; (b) A. R. Rezvani, C. Bensimon, B. Crompt, C. Reber, J. E. Greedan, V. V. Kondratiev and R. J. Crutchley, *Inorg. Chem.*, 1997, 36, 3322
- 5 (a) I. S. Moreira and D. W. Franco, *J. Chem. Soc., Chem. Commun.*, 1992, 450; (b) I. S. Moreira and D. W. Franco, *Inorg. Chem.*, 1994, 33, 1607
- 6 (a) N. Le Narvor and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1993, 357; (b) N. Le Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, 117, 7129; (c) F. Coat and C. Lapinte, *Organometallics*, 1996, 15, 477
- 7 T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, 35, 414
- 8 (a) V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 2705; (b) A. Harriman and R. Ziessel, *Chem. Commun.*, 1996, 1707; (c) V. Grosshenny, A. Harriman, M. Hissler and R. Ziessel, *Platinum Metals Rev.*, 1996, 40, 26 and 72
- 9 J. E. Sutton and H. Taube, *Inorg. Chem.*, 1981, 20, 3125
- 10 V. Grosshenny, A. Harriman, F. M. Romero and R. Ziessel, *J. Phys. Chem.*, 1996, 100, 17472
- 11 (a) A. Endo, Y. Hoshino, K. Hirakata, Y. Takeuchi, K. Shimizu, Y. Furushima, H. Ikeuchi and G. P. Sató, *Bull. Chem. Soc. Jpn.*, 1989, 62, 709; (b) Y. Hoshino, Y. Yukawa, T. Maruyama, A. Endo, K. Shimizu and G. P. Sató, *Inorg. Chim. Acta*, 1988, 150, 25
- 12 R. C. Mehrotra, R. Bohra and D. P. Gaur, "Metal β -Diketonates and Allied Derivatives", Academic Press, London, 1978, p. 31
- 13 Y. Kasahara, Y. Hoshino, M. Kajitani, K. Shimizu and G. P. Sató, *Organometallics*, 1992, 11, 1968
- 14 A. S. Hay, *J. Org. Chem.*, 1962, 27, 3320
- 15 Y. Hoshino, T. Nishikawa, K. Takahashi and K. Aoki, *Denki Kagaku Oyobi Kogyobutsuri Kagaku*, 1993, 61, 770
- 16 Y. Hoshino, T. Suzuki and H. Umeda, *Inorg. Chim. Acta*, 1996, 245, 87
- 17 G. L. Closs and J. R. Miller, *Science*, 1988, 240, 440
- 18 Y. Hoshino and Y. Hagihara, *Inorg. Chim. Acta*, 1999, 292, 64
- 19 (a) R. A. Marcus, *J. Chem. Phys.*, 1956, 24, 966; (b) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, 15, 155; (c) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, 811, 265; (d) R. A. Marcus and P. Siders, *J. Phys. Chem.*, 1982, 86, 622; (e) R. A. Marcus, and N. Sutin, *Inorg. Chem.*, 1975, 14, 213; (f) N. Sutin, *J. Photochem.*, 1979, 10, 19; (g) N. S. Hush, *Prog. Inorg. Chem.*, 1967, 8, 391; (h) N. S. Hush, *Electrochim. Acta*, 1968, 13, 1005; (i) N. S. Hush, *Coord. Chem. Rev.*, 1985, 64, 135
- 20 (a) B. E. Bowler, A. L. Raphael and H. B. Gray, *Prog. Inorg. Chem.*, 1990, 38, 259; (b) R. Kosloff and M. A. Ratner, *Israel J. Chem.*, 1990, 30, 45; (c) M. D. Newton, *Chem. Rev.*, 1991, 91, 767
- 21 A distance required by Hush theory is the effective donor-acceptor separation distance (r), assumed to be related to dipole moment expectation values by $r = |\mu_i - \mu_f|/\epsilon n$, where μ_i and μ_f are the dipole moments of the localised initial and final states in a mixed-valence system, respectively, and where ϵ is the electronic charge and n is the number of electrons in the system. On the other hand, R in Equation (viii) derived by the superexchange mechanism may be defined in terms of the actual bond lengths for the through-bond sequence pertinent to the pathway being modelled (20c). The Ru-Ru separation ($d(M-M)$) approximately reflects the length of the bridge in the present systems. In Class II binuclear metal complexes, when the metal-metal coupling is not very strong (probably $K_c < 10^4$), the metal-metal separation is usually used instead of the dipole moment length (24).
- 22 Y. Hoshino, H. Umeda and Y. Kamo, Abstracts of papers at the 44th Symp. on Coordination Chemistry of Japan, Yokohama, 1994, p. 178
- 23 T. Hashimoto, A. Endo, N. Nagao, G. P. Sató, K. Natarajan and K. Shimizu, *Inorg. Chem.*, 1998, 37, 5211
- 24 (a) S. S. Isied, A. Vassilian, J. F. Wishart, C. Creutz, H. A. Schwarz and N. Sutin, *J. Am. Chem. Soc.*, 1988, 110, 635; (b) M.-A. Haga, Md. M. Ali, S. Koseki, A. Yoshimura, K. Nozaki and T. Ohno, *Inorg. Chim. Acta*, 1994, 226, 17; (c) A.-C. Ribou, J.-P. Launay, K. Takahashi, T. Nihira, S. Tarutani and C. W. Spangler, *Inorg. Chem.*, 1994, 33, 1325; (d) A. R. Rezvani, C. Bensimon, B. Crompt, C. Reber, J. E. Greedan, V. V. Kondratiev and R. J. Crutchley, *Inorg. Chem.*, 1997, 36, 3322; (e) Y. J. Chen, C.-H. Kao, S. J. Lin, C.-C. Tai and K. S. Kwan, *Inorg. Chem.*, 2000, 39, 189; (f) R. C. Rocha, K. Araki and H. E. Toma, *Inorg. Chim. Acta*, 1999, 285, 197; (g) K. D. Demadis, G. A. Neyhart, E. M. Kober, P. S. White and T. J. Meyer, *Inorg. Chem.*, 1999, 38, 5948

The Author

Yoshimasa Hoshino is an Associate Professor in the Department of Chemistry, Faculty of Education, Nagasaki University, Japan. His main interests are in the molecular design of binuclear and polynuclear metal complexes with strong metal-to-metal communication and of rotaxane and polyrotaxane metal complexes for molecular switches.

Rapid Synthesis of Colloidal Clusters

Scientists from PCLCC, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, have synthesised uniform and stable polymer-stabilised colloidal clusters of platinum, iridium, rhodium, palladium, ruthenium and gold by microwave irradiation (W. Tu and H. Liu, *J. Mater. Chem.*, 2000, 10, (9), 2207–2211). As microwave heating has uniform and fast heating characteristics only a short irradiation time was needed. The colloidal clusters formed have small average diameters and narrow size distributions. Stable colloidal ruthenium clusters without boron were prepared using ethylene glycol as the reductant.