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Syntheses, crystal structure and electrochemical properties of dinuclear ruthenium complexes containing saturated and unsaturated spacers†

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Binuclear ruthenium complexes with two Ru(bpy)$_2$(PyCHN) units, where bpy = 2,2′-bipyridine and PyCHN = *N*-2-pyridylmethylene, linked together either directly or *via* spacers of variable length and nature have been prepared and characterizated. Electrochemical studies revealed that the comproportionation constant K_c clearly decreased with an increase in the number of phenyl rings. While inserting oxygen atom between the two phenyl rings decreased the K_c value, interruption of saturated CH$_2$ groups increased K_c from 2.7×10^5 to 5.8×10^5. The binuclear ruthenium complex containing the saturated –OCH$_2$CH$_2$O– fragment between the two phenyl groups also gave a large K_c (1.2×10^4), indicating that interruption within the bridge played a significant role in influencing ΔE and K_c for the dinuclear ruthenium complexes. These results demonstrated that the Schiff-base bridging ligands were particularly efficient for mediating the metal–metal coupling and approached molecular wire behavior. X-Ray crystal structure analyses of the free ligand BL$_6$ and one of the ruthenium complexes, **1**, are also reported.

Introduction

Long-range electron transfer reactions are of considerable importance in many areas of chemistry, ranging from bioinorganic chemistry to artificial molecular electronic devices, such as investigations of electron transfer in redox proteins[1] and chemical–electrical signal conversion for making biosensors.[2] As a model of an intramolecular electron-transfer reaction, the process of intervalence charge transfer in mixed-valence (MV) dinuclear complexes with various bridging ligands (BL) has been widely studied since the preparation of the Creutz–Taube ion,[3] and opened new fields of research: the chemistry and physics of mixed-valence compounds.[4] Furthermore, since mixed-valence compounds can be conductive,[5] as well as exhibiting significant nonlinear optical[6] and magnetic properties,[7] they are suggested in the design of electrochromic devices, solar energy conversion catalysts, photo-induced magnetic memory devices, chemical sensors and molecular-scale rectifiers.[8,9]

For the reasons above, there is still intensive activity in this field and to date a number of dinuclear MV compounds with large metal–metal separations have been prepared and studied. For some series of binuclear complexes with $[\mathrm{Ru(NH_3)_5}]^{2+}$ end groups, it is apparent that the extent of the metal–metal interaction decreases steadily as the π-overlap between the two halves of the bridging ligand decrease, which occurs when the ligand is lengthened, twisted, or contains a saturated fragment.[10,11] Investigations of mixed-valence dinuclear complexes incorporating saturated, rigid and spiro-fused rings with metal–metal separation ranging from 11.3 to 17.5 Å revealed that the comporprotationation constants K_c were all close to 4 and that the electronic coupling parameters V_{ab} decreased from 113 to 22 cm^{-1}, typical for weakly coupled systems.[12] Studies also exhibited that inserting a –CH$_2$– group within a 4,4′-bipyridine in $[\{\mathrm{Ru(NH_3)_5}\}_2(\mu\text{-4,4-bipyridine})]^{5+}$ gave K_c of 6.7. Though the disulfide bridge of a 4,4′-dithiobipyridine linker was surprisingly effective at mediating metal–metal interactions, due to the strong p(π)–d(π) interaction between the pyridyl rings and their sulfur atoms,[13] it is necessary to achieve strong coupling mixed-valence compounds with large metal–metal separation.

On the other hand, the Creutz–Newton–Sutin (CNS) model[14,15] and superexchange mechanism[16,17] recognized that metal–ligand interactions played a key role in metal–metal interactions, and the requirement to achieve a strong electronic interaction was to match the energy of the metal-based redox orbital with an appropriate bridging ligand (BL) orbital.[18] In this case, it should be expected that by proper choice of the terminal groups and the bridging ligand, one can obtain strong coupling mixed-valence compounds with large metal–metal separation[16] even when inserting a saturated fragment within the spacer. In fact, for biological systems, such as chloroplasts of mitochondria, electron-transfer reactions along a sequential redox chain occur very efficiently over a long distance through helical peptide bonds.[19,20] Here we designed and synthesized a series of dinuclear ruthenium complexes of the type [Ru(bpy)$_2$(PyCHN)]$_2$, with bpy = 2,2′-bipyridine and PyCHN = *N*-2-pyridylimine, in which the two pyridylimine ligands are interlinked at the imine nitrogen atom, either directly (BL$_1$, Scheme 1) or through a spacer of variable length (BL$_2$–BL$_6$).

Results and discussion

Syntheses and characterization of the ruthenium complexes

The bridging ligands, *N*,*N*′-bis(2-pyridylmethylene)azine[21] (BL$_1$), 1,4-bis(2-pyridylmethyleneamino)benzene[22] (BL$_2$), 4,4′-bis(2-pyridylmethylamino)bibenzene[23] (BL$_3$), bis[4-(2-pyridylmethyleneamino)phenyl] ether[24] (BL$_4$), bis[4-(2-pyridyl-

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† Electronic supplementary information (ESI) available: ORTEP of ligand BL$_6$. See http://www.rsc.org/suppdata/nj/b5/b502656c/

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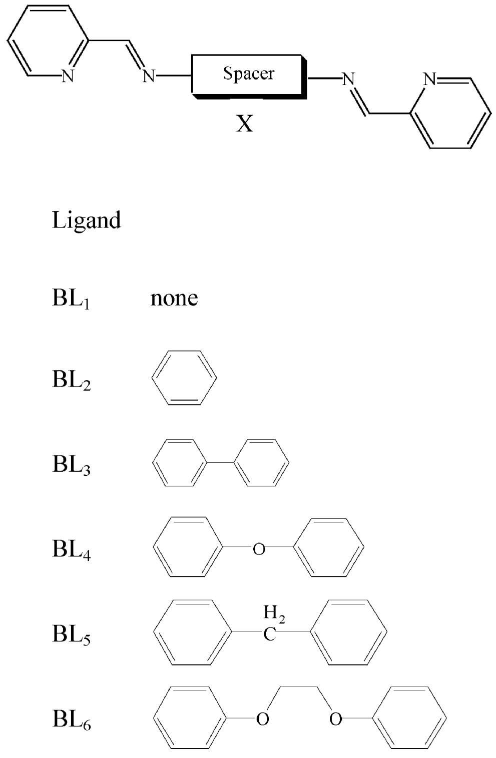

Scheme 1

methyleneamino)phenyl]methane[25] (BL_5), were prepared according to the literature method. The simplicity of the syntheses and the high yields in a single step from inexpensive commercially available reagents offer us the possibility to systematically probe the effects on the electron coupling when modifying the ligand backbone. The new Schiff-base ligand BL_6 was synthesized by reaction of bis(4-aminophenoxyl)ethane and 2-pyridinecarbaldehyde in methanol solution (Fig. 1). Evaporating the acetonitrile solution of the ligand BL_6 gave pale-yellow crystals suitable for crystal structure analysis. Elemental analyses, spectroscopic characterization, ^{1}H NMR and single crystal structure analysis confirmed the formation of the bis-bidentate ligand. As shown in Fig. 1, the ligand BL_6 has centric symmetry with the middle of the molecule positioned at the inversion center (see ESI†). Bond distances and angles were within normal ranges of similar compounds.[20–24]

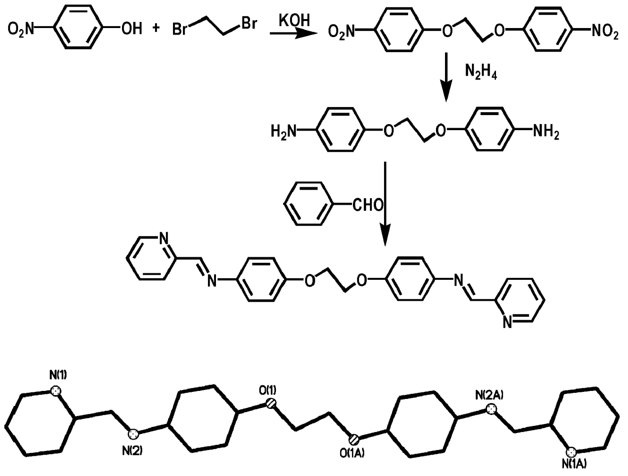

Fig. 1 Synthesis process and molecular structure of the free ligand BL_6; hydrogen atoms omitted for clarity, symmetry code: A = $1 - x$, $1 - y$, $1 - z$.

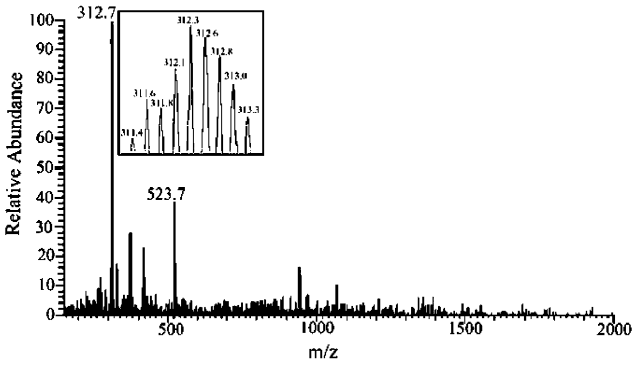

Fig. 2 Electrospray mass spectra of complex **6** in acetontrile solution. The inset shows the isotopic distribution for the base peak.

Reactions of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and the bridging ligands BL_1–BL_6 in ethanol solution gave the dinuclear ruthenium complexes **1**–**6**, in the presence of $NaClO_4$ or $NaBPh_4$. Elemental analyses and IR spectra were consistent well with the formation of dinuclear systems. ESI-MS spectra of these complexes exhibited the corresponding +4 charged $[\{(bipy)_2Ru\}_2(\mu\text{-}BL)]$ cation. Fig. 2 shows the ESI-MS spectra of complex **6**. Clearly, the main peak at m/z 312.7 was assigned to $[\{Ru(bpy)_2\}_2(\mu\text{-}BL_6)]^{4+}$, and another peak at m/z 523.7 was assigned to $[\{Ru(bpy)_2\}_2(\mu\text{-}BL_6)(BPh_4)]^{3+}$ for complex **6** in acetontrile solution (Fig. 2). It was suggested that the dinuclear species should be stable in the solution. UV-Vis spectra of these diruthenium complexes exhibited ligand-centered π–π* transitions at about 290 nm, and metal-to-terminal ligands and metal-to-bridging ligand dπ–π* orbital charge transfer (MLCT) transitions in the visible region (400–500 nm).[26,27] These bands were closely spaced and overlapped, it was difficult to separate one from another as observed for other mixed-ligand diimine complexes.[28,29]

An X-ray crystallographic study for complex **1** has unequivocally confirmed the existence of a dinuclear ruthenium species. The molecular structure of the cation of complex **1** is shown in Fig. 3. The asymmetric unit consisted half of the dinuclear complex, two disordered perchlorate anions, one disordered methanol molecule and one water molecule. The molecule of complex **1** had C_2 symmetry with the two ruthenium centres exhibiting the same absolute conformations. The Schiff -base ligand linked the two ruthenium centres with an Ru···Ru separation of 5.03 Å. The Ru^{II} ions were six-coordinated with two bpy chelates and the pyridylimine chelating unit from the bridging ligand. As shown in Table 1, The Ru–N distances of 2.021(6)–1.988(6) Å were within the normal ranges. The dihedral angle of the two pyridylimine based parts

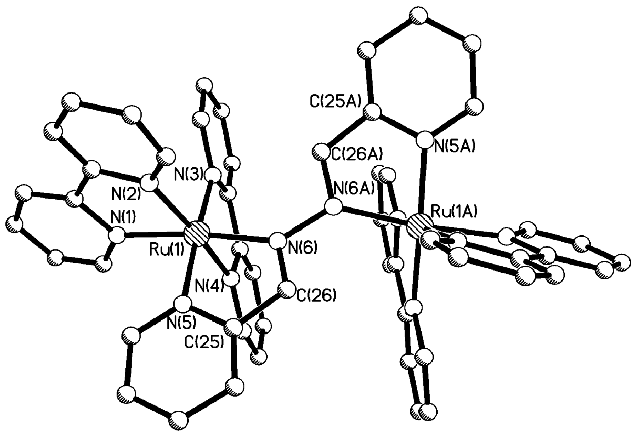

Fig. 3 Molecular structure of complex **1** showing the atomic-numbering scheme; hydrogen atoms, solvent molecules and the anions are omitted for clarity. Symmetry code: A = $2 - x$, $0.5 + y$, $1.5 - z$.

Table 1 Selected bond lengths (Å) and angles (°) of complex **1**[a]

Ru(1)–N(1)	2.021(6)	Ru(1)–N(2)	2.006(6)
Ru(1)–N(3)	1.988(6)	Ru(1)–N(4)	2.016(7)
Ru(1)–N(5)	2.007(5)	Ru(1)–N(6)	2.017(6)
N(6)–C(26)	1.280(8)	N(6)–N(6A)	1.468(10)
N(3)–Ru(1)–N(2)	96.9(2)	N(3)–Ru(1)–N(5)	173.2(3)
N(2)–Ru(1)–N(5)	89.7(2)	N(3)–Ru(1)–N(4)	78.9(2)
N(2)–Ru(1)–N(4)	170.6(2)	N(5)–Ru(1)–N(4)	94.3(2)
N(3)–Ru(1)–N(6)	101.9(2)	N(2)–Ru(1)–N(6)	102.0(2)
N(5)–Ru(1)–N(6)	78.2(2)	N(4)–Ru(1)–N(6)	87.1(2)
N(3)–Ru(1)–N(1)	84.1(2)	N(2)–Ru(1)–N(1)	78.8(2)
N(5)–Ru(1)–N(1)	95.6(2)	N(4)–Ru(1)–N(1)	92.3(2)
N(6)–Ru(1)–N(1)	173.7(2)		

[a] Symmetry code A: 2 − x, 0.5 + y, 1.5 − z.

of the ligand was *ca.* 22.3°. Although the whole ligand was not planar, the small twist angle indicated the considerable electronic delocalization of the whole π-conjugate system. It should be noted that the short Ru···Ru separation and the electronic delocalization of the bridging ligand might be important for the effective interaction of the two metal centers.

Electrochemistry

Differential pulse voltammetry (DPV) was employed to obtain well-resolved potential information, because the individual redox processes for the multi-nuclear complexes were poorly resolved in the CV experiment, in which individual $E_{1/2}$ potentials can not be easily or accurately extracted from this data.[30] DPV measurements of the six diruthenium complexes were obtained in acetontrile solution. The redox potentials are listed in Table 2. Fig. 4 shows typical spectra of complexes **2** and **3** from which it is clear that there are two main peaks at half-potential of 0.98 and 1.35 V *vs.* SCE for complex **2**. Because the ligand BL$_2$ did not exhibit any obvious peaks at 0–1.5 V under the DPV condition, the two peaks are assigned to $Ru^{III}Ru^{II}/Ru^{II}Ru^{II}$ and $Ru^{III}Ru^{III}/Ru^{III}Ru^{II}$ couples, with separation $\Delta E = 0.37$ V. For complex **3**, two peaks at 0.97 and 1.29 V based on the metal-centers were observed with lower value of ΔE (0.32 V), indicating that the extent of the metal–metal coupling is a little different in the two complexes.

As far as we are aware, the existence of any mixed-valence "intermediate" state is characterized by the comproportionation constant K_c according to eqns. (1) and (2).[31] K_c is simply the equilibrium constant for the reaction in eqn. (1). Provided the interaction is moderately strong, the value of K_c is simply determined from electrochemical data as expressed in eqn. (2). A high K_c may suggest that the mixed-valence complex can be prepared and studied effectively from its complete reduction and oxidation sates. Even with a low K_c, the mixed-valence may be generated either electrochemically or chemically.

$$[Ru^{II}Ru^{II}] + [Ru^{III}Ru^{III}] \rightleftharpoons 2[Ru^{II}Ru^{III}] \qquad (1)$$

Table 2 DPV data for complexes **1**–**6** in MeCN at room temperature

Compound	$E_{1/2}$/V	$E_{1/2}$/V	$\Delta E_{1/2}$/V	K_c	d_{Ru-Ru}/Å
1	0.86	1.43	0.57	4.6×10^9	5
2	0.98	1.35	0.37	2.0×10^6	9
3	0.97	1.29	0.32	2.7×10^5	13
4	0.99	1.16	0.17	7.6×10^2	13
5	0.99	1.33	0.34	5.8×10^5	13
6	1.00	1.24	0.24	1.2×10^4	15
Ru$_2$(bptz)[32]	1.52	2.02	0.50	3.0×10^8	7
Ru$_2$(apy)[33]	1.67	2.22	0.55	2.1×10^9	5
Ru$_2$(bpym)[35]	1.53	1.69	0.16	520	5
Ru$_2$(tpbq)[37]	1.43	1.60	0.17	760	7

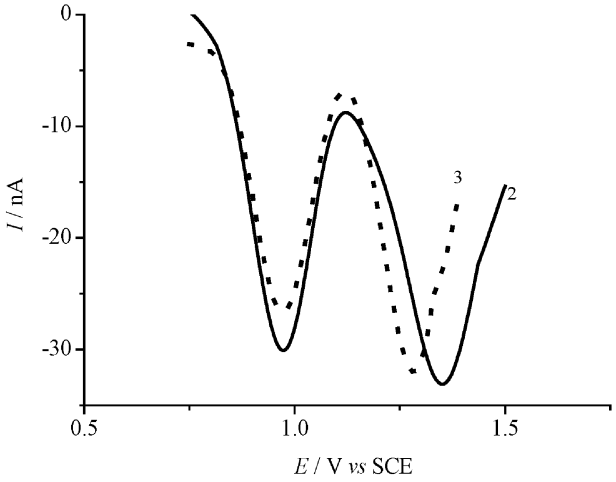

Fig. 4 Typical differential pulse voltammetry of complexes **2** and **3** in acetonitrile (1.0×10^{-3} M) at a scan rate of 20 mV s^{-1}. The supporting electrolyte is Bu$_4$NClO$_4$ (0.1 mol cm^{-3}).

$$K_c = 10^{\Delta E/59\,\mathrm{mV}} = [Ru^{II}Ru^{III}]^2/[Ru^{II}Ru^{II}][Ru^{III}Ru^{III}] \qquad (2)$$

As shown in Table 2, for complexes **1**, **2** and **3**, the ΔE and K_c values decreased, the latter from 10^9 to 10^5 as the Ru···Ru separation increased from 5 to 13 Å, indicating that the metal–metal separation was the main factor controlling the values of ΔE and K_c. Compared to complex **3**, ΔE and K_c of **4** decreased significantly, while those of **5** increased slightly. It seems that modifying the conjugated bridge was also significant in influencing ΔE and K_c for the dinuclear ruthenium complexes.

The ΔE and K_c values for dinuclear ruthenium complexes with two ending Ru(bpy)$_2$ groups linked by bisbidentate ligands have been reported elsewhere. The dinuclear ruthenium complexes linked by the ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz)[32] and aza-bis(2-pyridine) (apy)[33,34] exhibited larger ΔE (Table 2), while the complexes with bridging ligands such as 2,2′-bipyrimidine (bpym)[35,36] and tpbq (2,2′,3,3′-tetra(2-pyridyl)-6,6′-biquinoxaline)[37] gave smaller ΔE. Comparing to those of binuclear cyclometallated ruthenium complexes (K_c range from 4 to 1000) with metal–metal distances (d_{Ru-Ru}) ranging from 13.7 to 20.7 Å),[38,39] the potential separation (0.24 V) and K_c (1.2×10^4) for complex **6** are surprising. Considering the saturated –OCH$_2$CH$_2$O– group within the spacer, **6** is provided with increased flexibility, in fact, the two metal sites could be closer in space than those for other complexes. This is an important factor determining the ΔE and K_c. In general, the Schiff-base bridging ligands were particularly efficient for mediating the metal–metal coupling and approached molecular wire behavior.

In order to obtain more detailed information about the electronic interaction between the two Ru centers in this type of complexes, near-IR-vis spectra of the complexes upon chemical oxidation[40] were measured. Fig. 5 shows typical spectra of the step-by-step oxidation for the most interesting complex **4**. Upon oxidation, the intensity of the strong visible bands at about 420 and 450 nm due to MLCT decreased, and a new broad absorption band at about 700 nm appeared. Further addition of oxidant did not produce any other obvious bands, until three-times excess oxidant was added. The moderately broad band at 600–800 nm is probaly assignable to the LMCT of the π(bpy) to t$_{2g}$(Ru^{III}) transition.[41] Spectra were recorded out to 2800 nm in the NIR to investigate the presence of any intervalence charge transfer transition. An exceedingly weak feature appeared in the range of 1500–2200 nm. Other compounds exhibited similar spectra during the oxidation processes. The NIR-vis spectral data for complexes **1**–**6** are shown in Table 3. The values of V_{ab} (the electronic coupling parameter) of the complexes can not be calculated from the

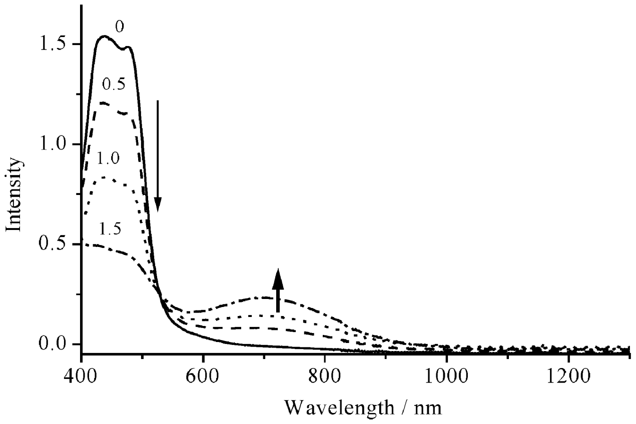

Fig. 5 Typical NIR-vis spectra of complex **4** (1.0×10^{-5} M) upon the addition of oxidant Ce(IV), the numbers indicating equivalents of the oxidant added.

Table 3 NIR-vis spectral data for complexes **1**–**6** in acetonitrile solution at room temperature

Compound	ν_{LMCT}/cm^{-1}	$\varepsilon/M^{-1}\ cm^{-1}$	$\nu_{1/2}/cm^{-1}$	V_{ab}/cm^{-1}
$\mathbf{1}^{5+}$	13 100	3030	3600	1600
$\mathbf{2}^{5+}$	14 900	3330	4000	760
$\mathbf{3}^{5+}$	14 300	1800	5800	300
$\mathbf{4}^{5+}$	14 200	4000	4500	220
$\mathbf{5}^{5+}$	14 000	2500	6500	560
$\mathbf{6}^{5+}$	13 000	3200	4800	350

Hush formula due to the weak absorption. However, the CNS model[14,15] can be used to calculate the coupling elements of the six compounds from the data and eqns. (3) and (4).

$$V_{ab} = H_{ML}^2/2\Delta E_{ML} + H_{LM}^2/\Delta E_{LM} \quad (3)$$

$$1/\Delta E_{ML} = 1/2\Delta E_{MLCT} + 1/2(\Delta E_{MLCT} - \Delta E_{MMCT}) \quad (4)$$

In eqns. (3) and (4), H_{ML} is the metal–ligand coupling for the Ru^{II} site (determined by the intensity and position of the MLCT band by an equation used to calculate V_{ab} for the MMCT band) and ΔE_{ML} is the effective energy gap; ΔE_{MLCT} and ΔE_{MMCT} are the positions of the MLCT and metal-to-metal (intervalence) transitions, respectively. This procedure requires mainly the recording of the charge transfer transitions, and that the intervalence transition intervenes only by its position, which can be only approximately determined. In our system, the MMCT band is determined as 2000 nm. The calculated values of V_{ab} for the MMCT are listed in Table 3. As one can see, the extent of the metal–metal coupling resulting from the values V_{ab} is well consistent with that from ΔE in the electrochemical measurements. In the π-conjugated systems (from **1** to **3**), the extent of the metal–metal coupling decreased with the metal–metal distance increasing. However, interrupting the conjugated system may increase the metal–metal interaction, because the two metal sites could be closer in space due to the increased flexibility of the bridging ligand.

Conclusions

The present series of complexes exhibited strong metal–metal interactions and approach molecular wire behavior even for the spacer containing the $-OCH_2CH_2O-$ fragment. The detailed comparison of K_c values as a function of metal–metal distances revealed that inserting the CH_2 group within the phenyl rings increases K_c, and that an inserting oxygen atom decreases K_c, the metal–metal separation and mediating conjugation seem to play a significant role in determining K_c.

Experimental

Materials and methods

The bridging ligands, *N*,*N*′-bis(2-pyridylmethylene)azine[20] BL$_1$, 1,4-bis(2-pyridylmethyleneamino)benzene[21] BL$_2$, 4,4′-bis(2-pyridylmethylamino)bibenzene[22] BL$_3$, bis[4-(2-pyridylmethyleneamino)phenyl]methane[23] BL$_4$, bis[4-(2-pyridylmethyleneamino)phenyl] ether[24] BL$_5$ and *cis*-Ru(bpy)$_2$Cl$_2$ · 2H$_2$O were prepared as described in the literature.[42] All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Electrospray mass spectra were carried out on a LCQ system (Finnigan MAT, USA) using methanol as mobile phase. Electronic absorption spectra were obtained at room temperature on a Shimadzu 3100 spectrophotometer in acetonitrile solution. Differential pulse voltammetry (DPV) was done with an EG and GPAR model 273 instrument in a three-electrode cell with a pure Ar gas inlet and outlet. The working electrode and counter electrode were Pt spirals, and the reference electrode was a saturated calomel electrode (SCE). The experiments were carried out in CH_3CN solution with Bu_4NClO_4 (0.1 M). DPV experiments were performed with a scan rate of 20 mV s^{-1}. NIR-vis spectra were recorded in a 1 cm quartz cell with a Perkin-Elmer Lambda 19 spectrophotometer. The mixed-valence species were obtained by successive stoichiometric additions of Ce(IV) according to the literature.[40]

Syntheses

CAUTION! Although no problems were encountered in this work, perchlorates are potentially explosive, and should be handled with care.

BL$_6$. 1,2-Bis(4-aminophenoxyl)ethane (0.45 g, 1.8 mmol) and 2-pyridinecarbaldehyde (0.5 g, 3.6 mmol) were mixed in ethanol (25 mL) and refluxed for 3 h. The pale yellow solid (0.5 g, 1.2 mmol, yield 67%) was filtered off and dried under vacuum. Found: C, 73.9; H, 5.8; N, 13.7. Calc. for $C_{26}H_{22}N_4O_2$: C, 73.9; H, 5.3; N, 13.3%. ^{1}H NMR: δ 8.68 (2H, py, d), 8.61 (2H, CH, s), 8.12 (2H, py, d), 7.92 (2H, py, m), 7.49 (2H, py, m), 7.38 (4H, Ph, d), 7.06 (4H, Ph, d), 4.36 (4H, $-CH_2$, s). IR (cm^{-1}): 3060 (ν_{C-H}), 1625, 1578, 1476, 1463, 1279 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 1243, 1279 (ν_{Ph-O}), 833, 777, 739 (δ_{C-H}).

[{Ru(bpy)$_2$}$_2$(μ-BL$_1$)](ClO$_4$)$_4$ 1. An ethanol solution of AgNO$_3$ (0.10 g, 0.62 mmol) was added to an ethanol solution of [Ru(bpy)$_2$Cl$_2$] · 2H$_2$O (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL$_1$ (0.03 g, 0.16 mmol) was added and the solution was refluxed for 12 h under N$_2$. Complex **1** separated as a red precipitate, which was collected by filtration, washed with ethanol several times, dried in vacuum over P$_4$O$_{10}$, and gave the product (0.15 g, 68%). Anal. Calc. for $C_{52}H_{42}N_{12}Ru_2 \cdot 4ClO_4$: C, 43.5; H, 3.0; N, 11.7. Found: C, 43.6; H, 3.2; N, 11.6%. IR (cm^{-1}): 3402 (ν_{C-H}), 1612, 1546, 1423 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 858, 746, 560 (δ_{C-H}).

[{Ru(bpy)$_2$}$_2$(μ-BL$_2$)](ClO$_4$)$_4$ 2. An ethanol solution of AgNO$_3$ (0.10 g, 0.62 mmol) was added to an ethanol solution of [Ru(bpy)$_2$Cl$_2$] · 2H$_2$O (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL$_2$ (0.05 g, 0.16 mmol) was added and the solution was refluxed for 12 h under N$_2$. Complex **2** separated as a orange precipitate, which was collected by filtration, dried in vacuum over P$_4$O$_{10}$, and gave the product (0.16 g, 71%). Anal. Calc. for

$C_{58}N_{12}H_{46}Ru_2Cl_4O_{16}$: C, 46.1; H, 3.1; N, 11.1; Found: C, 46.3; H, 3.0; N, 11.1%. IR (cm^{-1}): 3448 ($\nu_{C\text{–}H}$), 1618, 1508, 1463 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C\text{–}N}$), 843, 731, 705 ($\delta_{C\text{–}H}$).

[{Ru(bpy)$_2$}$_2$(μ-BL$_3$)](BPh$_4$)$_4$ 3. An ethanol solution of $AgNO_3$ (0.10 g, 0.62 mmol) was added to an ethanol solution of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL_3 (0.054 g, 0.15 mmol) was added and the solution was refluxed for 12 h under N_2. Complex **3** separated as a yellow precipitate. The product were purified by dissolving the precipitate in DMF, then added this to ethanol, to yield an orange powder. The powder was washed with ethanol three times and dried in vacuum over P_4O_{10}, to gave the product (0.24 g, 65%). Anal. Calc. for $C_{64}H_{50}N_{12}Ru_2\cdot 4BPh_4$: C, 77.8; H, 5.3; N, 6.8. Found: C, 77.8; H, 5.3; N, 7.0%. IR (cm^{-1}): 3445 ($\nu_{C\text{–}H}$), 1636, 1523, 1445 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C\text{–}N}$), 833, 766, 730 ($\delta_{C\text{–}H}$).

[{Ru(bpy)$_2$}$_2$(μ-BL$_4$)](BPh$_4$)$_4$ 4. A procedure similar to that described for complex **2** was followed: an ethanol solution of $AgNO_3$ (0.10 g, 0.62 mmol) was added to an ethanol solution of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL_4 (0.06 g, 0.15 mmol) was added and the solution was refluxed for 12 h under N_2. An orange precipitate was formed when adding the solution to an ethanol solution of $NaBPh_4$. The product was purified by dissolving the precipitate in DMF, then added to ethanol, yielding a yellow powder. The powder was washed with ethanol three times and dried in vacuum over P_4O_{10}. Yield 0.29 g (77%). Anal. Calc. for $C_{64}H_{50}N_{12}ORu_2\cdot 4BPh_4$: C, 77.3; H, 5.3; N, 6.8. Found: C, 77.4; H, 5.5; N, 7.0%. IR (cm^{-1}): 3424 ($\nu_{C\text{–}H}$), 1603, 1532, 1468 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C\text{–}N}$), 833, 721, 560 ($\delta_{C\text{–}H}$).

[{Ru(bpy)$_2$}$_2$(μ-BL$_5$)](ClO$_4$)$_4$ 5. An ethanol solution of $AgNO_3$ (0.10 g, 0.62 mmol) was added to a ethanol solution of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL_5 (0.06 g, 0.15 mmol) was added and the solution was refluxed for 8 h under N_2. An orange precipitate was formed when adding the solution to a saturated ethanol solution of $NaClO_4$. Yield 0.19 g (76%). Anal. Calc. for $C_{65}N_{12}H_{52}Ru_2\cdot 4ClO_4$: N, 10.5; C, 48.8; H, 3.2. Found: N, 10.3; C, 48.8; H, 3.3%. IR (cm^{-1}): 3424 ($\nu_{C\text{–}H}$), 1603, 1508, 1466 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C\text{–}N}$), 769, 560 ($\delta_{C\text{–}H}$).

[{Ru(bpy)$_2$}$_2$(μ-BL$_6$)](BPh$_4$)$_4$ 6. An ethanol solution of $AgNO_3$ (0.10 g, 0.62 mmol) was added to a ethanol solution of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.17 g, 0.32 mmol). After refluxing for 30 min and filtering to remove the deposited AgCl, the ligand BL_6 (0.07 g, 0.16 mmol) was added and then refluxed for 8 h under N_2. An orange precipitate was formed when adding the solution to an ethanol solution of $NaBPh_4$. The product was purified by dissolving the precipitate in DMF, then reprecipitating with ethanol, to yield a yellow powder. The powder was washed with ethanol three times and dried in vacuum over P_4O_{10}. Yield 0.33 g (81%). Anal. Calc. for $C_{66}H_{54}N_{12}O_2Ru_2\cdot 4BPh_4$: C, 77.0; H, 5.4; N, 6.7. Found: C, 76.8; H, 5.3; N, 6.5%. IR (cm^{-1}): 444 ($\nu_{C\text{–}H}$), 1634, 1539, 1504, 1463 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C\text{–}N}$), 837, 770, 736 ($\delta_{C\text{–}H}$).

Crystallography

Parameters for data collection and refinement of complex **1** and the ligand BL_6 are summarized in Table 4. Intensities were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) using SMART and SAINT[43] programs. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.1.[44] Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculated positions and refined using a riding model.

Table 4 Crystallographic data for the ligand BL_6 and complex **1**

	$BL_6\cdot CH_3OH$	$\mathbf{1}\cdot CH_3OH\cdot H_2O$
Molecular formula	$C_{27}H_{26}N_4O_3$	$C_{53}H_{48}N_{12}O_{18}Ru_2Cl_4$
M	454.52	1484.00
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	13.477(3)	25.242(1)
b/Å	4.9491(9)	15.105(6)
c/Å	18.952(4)	17.269(7)
β/°	108.357(4)	98.179(6)
V/Å^3	1199.7(4)	6517(5)
Z	2	4
T/K	293(2)	293(2)
μ/mm^{-1}	0.084	0.706
No. reflections measured	2029	5418
No. unique reflections	1071	1635
R_1	0.0615	0.0687
wR_2	0.1608	0.1589

CCDC reference numbers 230148 and 230149.

See http://www.rsc.org/suppdata/nj/b5/b502656c/ for crystallographic data in CIF or other electronic format.

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