Organometallics 1992, *11*, 1968–1971

Synthesis of Binuclear (β-Diketonato)ruthenium(III) Complexes through Introduction of an Ethynyl Group at a γ-Position of Tris(β-diketonato)ruthenium(III) and Electrochemistry of the Binuclear Complexes

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Received September 13, 1991

Summary: An ethynyl group was introduced into a γ-position of a tris(β-diketonato)ruthenium(III) complex through the reaction of the complex and (trimethylsilyl)acetylene followed by removal of the trimethylsilyl group. The ethynyl complex is a useful intermediate for syntheses of homo- and heterobinuclear complexes. The preparation of two binuclear complexes, $[L_2Ru^{III}(OCMe)_2C(-C{\equiv}C-)_2C(MeCO)_2Ru^{III}L_2]$ and $[L_2Ru^{III}(OCMe)_2C(-C{\equiv}C-)_2Fc]$ ($L = [Me_3CCOCHCOCMe_3]^-$, Fc = ferrocenyl), is described. The homobinuclear complex underwent a stepwise two-electron oxidation and reduction through the Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II} states, respectively, in acetonitrile and dicholoromethane media at 25 °C. The stabilities of the mixed-valence states are briefly discussed in terms of the comproportionation constants.

Acetylenic compounds are useful synthetic intermediates because of their availability and versatility.[2] A terminal alkyne can form a bridging group between two metal atoms[3-7] or organometallic moieties.[8] In view of the quasi-aromatic reactivity of the γ-methine of a β-diketonato chelate ring, it should be possible to introduce an alkyne group at the γ-position and to make a bridge between two mononuclear chelates. No such synthesis, however, has yet been described, although instances are known of a wide variety of γ-substitution reactions (for example, halogenation, nitration, and acetylation).[9] We report here a new method for introducing an ethynyl group into a γ-position of tris(β-diketonato)ruthenium(III) and the syntheses of several homo- and heterobinuclear (β-diketonato)ruthenium complexes through coupling of the γ-ethynyl complexes. Electrochemical characteristics of new ethynyl mononuclear and binuclear complexes are also described.

Experimental Section

Measurements. Proton NMR spectra were determined as solutions in $CDCl_3$ ($SiMe_4$ as internal reference) with a JEOL GX-270 spectrometer. IR spectra and mass spectra were recorded with a JIR-3001 FT-IR spectrophotometer and JEOL JMS-D300 and JMS-SX102 spectrometers, respectively. Voltammograms of the complexes were recorded as described previously.[10] Acetonitrile containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) and dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) were used as base solutions. The test electrode was a stationary platinum disk (ϕ = 1.99 mm). The potentials were measured against a silver–silver ion reference electrode, Ag\|0.1 mol dm^{-3} $AgClO_4$–CH_3CN, unless otherwise stated. The ferrocenium/ferrocene potentials of the reference electrodes are presented in the corresponding tables.

Materials. Dichloromethane and acetonitrile (Wako, liquid chromatographic grade) were dried over Wako 4-Å molecular sieves for electrochemical measurements. TEAP and TBAP (both polarographic grade) were purchased from Nacalai Tesque, Inc. Triethylamine (Wako, reagent grade) was dried over potassium hydroxide. (Trimethylsilyl)acetylene, dichlorobis(triphenylphosphine)palladium(II), and 1 mol dm^{-3} tetrabutylammonium fluoride–tetrahydrofuran solution were purchased from Aldrich Chemical Co., Inc. All other solvents (reagent grade) were used without further purification.

Preparation of Complexes. Ethynylferrocene (Fc-ethy) and 1,4-diferrocenyl-1,3-butadiyne (Fc-buty-Fc) were obtained according to literature methods.[8] The starting material $[Ru(acac)(dpm)_2]$ (1; $acac^-$ = 2,4-pentanedionate ion and dpm^- = 2,2,6,6-tetramethyl-3,5-heptanedionate ion) was prepared by the "ruthenium blue solution" method[11,12] or by the substitution reaction of $[Ru(dpm)_2(CH_3CN)_2]^+$.[13]

The processes of introducing an ethynyl group into a γ-position of 1 are summarized in Scheme I.

$[Ru(mIma)(dpm)_2]$ (2; $mIma^-$ = 3-Iodo-2,4-pentanedionate Ion). This complex was prepared by the direct substitution of the 3-position of the acac ligand of 1.[14] *N*-Iodosuccinimide was added to a benzene solution of 1. The amount-of-substance ratio of the succinimide to 1 was 1.5. Purification of 2 was performed by column chromatography on Merck Kieselgel 60 with a mixture of benzene–hexane (1:1 by volume). A red solid was obtained after the solvent was evaporated off; yield 81%. Anal. Calcd for $C_{27}H_{44}O_6IRu$: C, 46.78; H, 6.35; M_r, 692.6. Found: C, 46.13; H, 6.45; M^+, 693 (EI). ^1H NMR ($CDCl_3$): δ −44.37 (s, 2 H, CH), −0.62 (s, 6 H, CH_3), 2.24 (s, 36 H, $C(CH_3)_3$).

$[Ru(mESima)(dpm)_2]$ (3; $mESima^-$ = 3-((Trimethylsilyl)ethynyl)-2,4-pentanedionate Ion). Introduction of an ethynyl group into the 3-position of the mIma ligand of 2 was performed according to a synthetic method for 1-alkynyl ketones[15] with slight modification. First, 30 cm^3 of triethylamine containing 100 mg (0.14 mmol) of 2 and 17 mg of (trimethylsilyl)acetylene were stirred under argon with dichlorobis(triphenylphosphine)palladium(II) and copper(I) iodide (2 mg each) as catalysts. When

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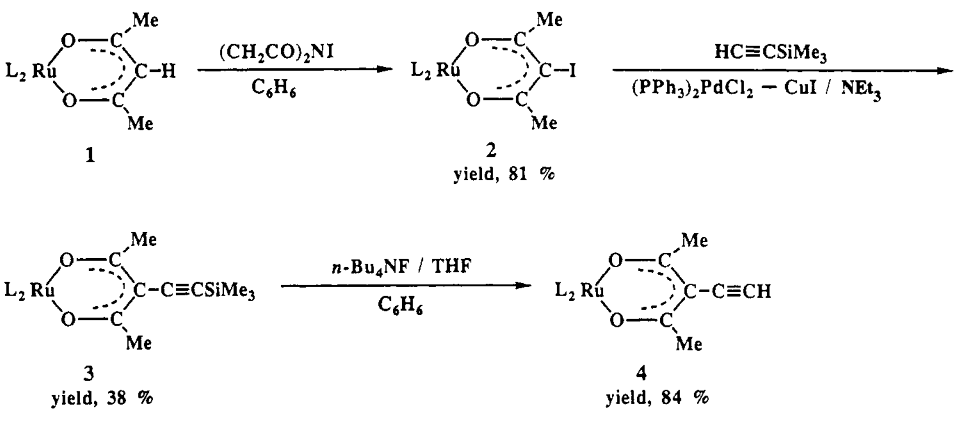
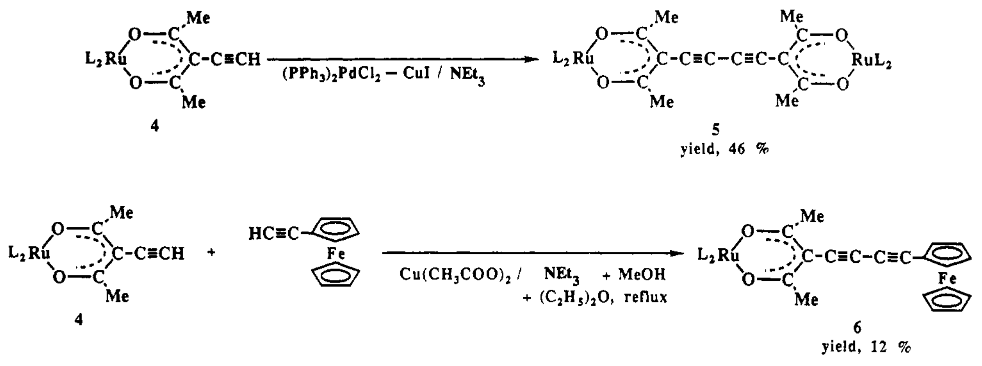
Scheme I



L = $[Me_3CCOCHCOCMe_3]^-$

Scheme II



L = $[Me_3CCOCHCOCMe_3]^-$

the reaction ceased, the same amounts of HC≡CSiMe$_3$ and the catalysts were added again to the mixture. This procedure was repeated three times (the total amount-of-substance ratio of HC≡CSiMe$_3$ to 2 was ca. 6); then the reaction mixture was stirred for 4 days at room temperature. The residue obtained after the removal of the solvent was extracted with a mixture of benzene–hexane (3:2 by volume). The extract was applied onto a column of Kieselgel 60, and the column was developed with the benzene–hexane mixture. The eluate of the first, purple-red band was collected. Complex 3 was obtained as a purple solid when the solvent was evaporated off; yield 38%. Anal. Calcd for $C_{32}H_{53}O_6SiRu$: C, 57.49; H, 8.03; M_r, 662.9. Found: C, 57.98; H, 8.06; M$^+$, 663 (EI). ^{1}H NMR (CDCl$_3$): δ −47.37 (s, 2 H, CH), 0.75 (s, 9 H, Si(CH$_3$)$_3$), 1.95 (s, 18 H, C(CH$_3$)$_3$), 2.90 (s, 18 H, C(CH$_3$)$_3$), 5.41 (s, 6 H, CH$_3$). IR (KBr): 2140 cm^{-1} (C≡C).

[Ru(mEma)(dpm)$_2$] (4; mEma$^-$ = 3-Ethynyl-2,4-pentanedionate Ion). Removal of the trimethylsilyl group of 3 was carried out by treating the complex with an excess (1.5 equiv) of tetrabutylammonium fluoride:[16] 0.4 cm^3 of 1 mol dm^{-3} Bu$_4$NF–THF solution was added to 200 mg of 3 dissolved in 50 cm^3 of benzene. After the solvent was removed by evaporation, the residue was subjected to chromatography on a column of Merck aluminum oxide 90 with a benzene–hexane mixture (1:2 by volume) in order to isolate 4, which was obtained as a red solid when the solvent was evaporated from the relevant fractions. Here, alumina had to be used, because 4 was readily converted to the corresponding acetyl derivative through the addition of water when it was in contact with silica. For the same reason, 4 was kept in a desiccator; yield 84%. Anal. Calcd for $C_{29}H_{45}O_6Ru$: C, 58.88; H, 7.61; M_r, 590.7. Found: C, 58.01; H, 7.81; M$^+$, 591 (EI). ^{1}H NMR (CDCl$_3$): δ −46.98 (s, 2 H, CH), −11.65 (s, 1 H, C≡CH), 2.03 (s, 18 H, C(CH$_3$)$_3$), 2.27 (s, 18 H, C(CH$_3$)$_3$), 4.17 (s, 6 H, CH$_3$). IR (KBr): 2100 cm^{-1} (C≡C).

The procedures of the syntheses of the binuclear complexes are summarized in Scheme II.

(μ-1,1,6,6-Tetraacetyl-2,4-hexadiynato)bis[bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III)] (5). To 50 cm^3 of triethylamine solution containing 200 mg (0.34 mmol) of 4 were added 0.34 mmol each of PdCl$_2$(PPh$_3$)$_2$ and CuI. The mixture was stirred at room temperature for several hours under argon, and then the solvent was evaporated off. The residue was applied onto a column of Kieselgel 60, and the column was developed with a benzene–hexane mixture (4:1 by volume). The eluate of the first, dark red band was evaporated to dryness, and the residue was recrystallized from a water–ethanol solution. Dark red crystals were obtained; yield 46%. Anal. Calcd for $C_{58}H_{88}O_{12}Ru_2$: C, 59.06; H, 7.52; M_r, 1180.4363. Found: C, 59.01; H, 7.51; M$^+$, 1180.3537 (FAB). ^{1}H NMR (CDCl$_3$): δ −47.76 (s, 4 H, CH), 2.01 (s, 36 H, C(CH$_3$)$_3$), 2.96 (s, 36 H, C(CH$_3$)$_3$), 5.90 (s, 12 H, CH$_3$). IR (KBr) 2140 cm^{-1} (C≡C).

{3-(4-Ferrocenyl-1,3-butadiynyl)-2,4-pentanedionato}bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III) (6). This binuclear complex was prepared according to the method of Schlögl.[8] Complex 4 (24 μmol, 14 mg) and Fc-ethy (24 μmol, 5.0 mg) were dissolved in ca. 20 cm^3 of diethyl ether–methanol–triethylamine (10:4:5 by volume), and 48 μmol (8.7 mg) of bis(acetato)copper(II) was added to this solution. After the mixture was refluxed for 1 h, the solvent was evaporated off. The residue was subjected to column chromatography on Kieselgel 60 with benzene–hexane–chloroform (1:1:2 by volume). The red-brown eluate was collected and evaporated to dryness. The red-brown crystals were dried in vacuo; yield 12%. Anal. Calcd for $C_{41}H_{53}O_6FeRu$: M_r, 799.2235. Found: M$^+$, 799.2250 (FAB). ^{1}H NMR (CDCl$_3$): δ −49.06, (s, 2 H, CH), 2.01 (s, 18 H, C(CH$_3$)$_3$), 2.86 (s, 18 H, C(CH$_3$)$_3$), 4.28 (t, 2 H, Cp-α), 4.37 (s, 5 H, Cp), 4.58 (t, 2 H, Cp-β), 5.40 (s, 6 H, CH$_3$). IR (KBr): 2140, 2210 cm^{-1} (C≡C).

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Table I. Reversible Half-Wave Potentials ($E_{1/2}$) for the Mononuclear Complexes in 0.1 mol dm^{-3} TEAP–Acetonitrile at 25 °C^a

	$E_{1/2}$/V^b (ΔE_p/mV)^c		
complex	Ru^{III}/Ru^{II}	Ru^{IV}/Ru^{III}	Fe^{III}/Fe^{II}
1	−1.318 (65)	0.516 (61)	
2	−1.205 (66)	0.578 (69)	
3	−1.199 (113)^d	0.606 (65)	
4	−1.211 (69)	0.614 (60)	
[Ru(mAma)(dpm)$_2$]	−1.232 (104)^d	0.599 (88)	
Fc-H			0.025 (74)
Fc-ethyl			0.184 (65)

^{a} $E_{1/2}$ was determined by normal pulse voltammograms. ^{b} Potentials vs Ag|0.1 mol dm^{-3} AgClO$_4$ in CH$_3$CN. ^{c} Values in parentheses are triangular-wave voltammetric peak separations at a sweep rate of 0.1 V s^{-1}. ^{d} Quasi-Nernstian.

Table II. Reversible Half-Wave Potentials ($E_{1/2}$) for the Binuclear Complexes in 0.1 mol dm^{-3} TEAP–Acetonitrile at 25 °C^a

	Ru^{III}/Ru^{II} or Fe^{III}/Fe^{II}			Ru^{IV}/Ru^{III}		
complex	$E_{1/2}$/V^b		$\Delta E_{1/2}$/mV^c	$E_{1/2}$/V^b		$\Delta E_{1/2}$/mV^c
5	−1.141 −0.849^d	−1.219 −0.932^d	78 83	0.548 0.932^d	0.707 1.162^d	159 230
6	−1.157^e	0.195^f		0.660		
Fc-buty-Fc	0.190	0.284	94			

^{a} $E_{1/2}$ was determined by differential pulse voltammograms. ^{b} Potentials vs Ag|0.1 mol dm^{-3} AgClO$_4$ in CH$_3$CN. ^{c} $\Delta E_{1/2}$ was estimated from the peak half-width in the differential pulse voltammogram with use of the technique in ref 22. ^{d} Potentials were measured in 0.1 mol dm^{-3} TBAP–CH$_2$Cl$_2$ vs Ag|AgCl, KCl (saturated aqueous) at 25 °C. $E_{1/2}$(ferrocenium/ferrocene) = 0.550 V. ^{e} Couple of Ru^{III}/Ru^{II}. ^{f} Couple of Fe^{III}/Fe^{II}.

Results and Discussion

The iodination, an electrophilic substitution, occurred selectively at the γ-position of the acac ligand of 1 owing to the presence of the bulky *tert*-butyl substituents on the β-positions of the dpm ligands. It is noted that the reaction of 2 with HC≡CSiMe$_3$ was solvent-dependent; when triethylamine was replaced by diethylamine, the iodine was substituted mainly by hydrogen and then 1 was reproduced with small amounts of four unidentified compounds. Ethynyl complex 4 is a relatively active compound. Addition of a water molecule takes place at the ethynyl group, giving [Ru(mAma)(dpm)$_2$] (mAma$^-$ = 3-acetyl-2,4-pentanedionate ion)[17] when 4 is exposed to moisture or, particularly, it is subjected to silica gel chromatography as mentioned earlier.

Complex 4 did not undergo heterocoupling with 2 even though the reaction conditions used here were considered to favor the coupling between ethynyl and iodo-substituted carbon;[18] the reaction gave 5, instead of the ethynylene-bridged dimer, leaving 2 unreacted.

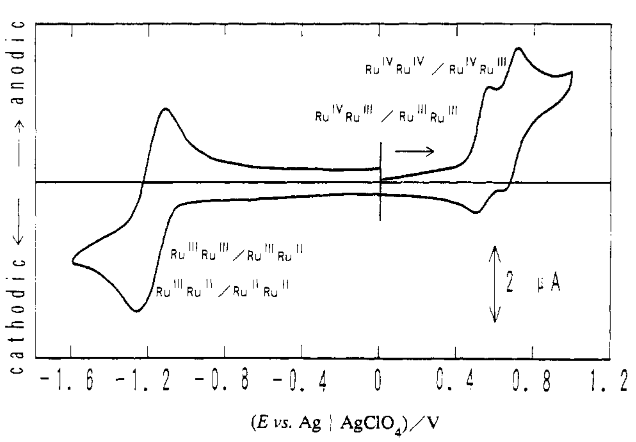

Figure 1. Triangular-wave voltammogram for a 0.25 mmol dm^{-3} solution of complex 5 in 0.1 mol dm^{-3} Et$_4$NClO$_4$–CH$_3$CN at 25 °C on a Pt-disk electrode (diameter 1.99 mm). The scan rate was 0.1 V s^{-1}.

Lewis and Sishta[19] reported that the reaction of vinylferrocene with [Ru(mIma)$_3$] yielded tris(ferrocenyl-substituted 2,4-pentanedionato)ruthenium(III), whereas an attempt at carrying out a similar reaction with [Co(mIma)$_3$] failed because a cyclization took place, leading to ferrocenyl-substituted dihydrofurans.[20] In the present preparation of 6 from Fc-ethy and 4, the yield of 6 was relatively low owing to the formation of 5 and Fc-buty-Fc.

The voltammetric characteristics of the mononuclear complexes and the binuclear complexes are presented in Tables I and II, respectively.

Each mononuclear ruthenium(III) complex showed an oxidation step and a reduction step in 0.1 mol dm^{-3} TEAP–CH$_3$CN on a Pt electrode at 25 °C. The analysis of the normal pulse voltammograms and the corresponding triangular-wave voltammograms indicated that the oxidation and the reduction steps were Nernstian one-electron processes without subsequent homogeneous reactions, except the reduction steps of 3 and [Ru(mAma)(dpm)$_2$]. The reduction steps of 3 and [Ru(mAma)(dpm)$_2$] were quasi-Nernstian, as indicated by the sweep-rate dependence of the triangular-wave voltammetric anodic (E_{pa}) and the cathodic (E_{pc}) peak potentials and the separation between them (ΔE_p). Fc-ethy showed only a Nernstian one-electron step.

The reversible half-wave potentials ($E_{1/2}$) of anodic steps of 2–4 and [Ru(mAma)(dpm)$_2$] are 62–98 mV more positive than that of 1; similarly, the $E_{1/2}$ values of their reduction steps are 86–119 mV more positive than that of 1. These positive shifts of the potentials reflect the electron-withdrawing character of –I, –C≡CSiMe$_3$, –C≡CH, and –COMe substituents. A similar positive shift was observed in the case of Fc-ethy as well. The $E_{1/2}$ value for Fc-ethy was shifted from that of Fc by +159 mV in acetonitrile, which is comparable to the shift observed in dichloromethane, +180 mV.[21]

A typical triangular-wave voltammogram of 5 in acetonitrile medium is shown in Figure 1. The two pairs of peaks on the positive side of the voltammogram correspond to two consecutive, Nernstian one-electron-oxidation steps. The pair of broader peaks at about −1.2 V is attributable to two overlapping reduction processes; the analysis of the corresponding normal pulse voltammogram showed that the reduction process consisted of two closely overlapping one-electron steps. The peak potentials were independent of the sweep rate, suggesting that both steps were Nernstian. Accordingly, the separation of their half-wave potentials, $\Delta E_{1/2}$, was estimated from the peak width of the differential pulse voltammogram.[22] The electrochemical behavior of 5 in dichloromethane was essentially the same as that in acetonitrile. The above observations

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[17] [Ru(mAma)(dpm)$_2$]: calcd M_r for C$_{29}$H$_{47}$O$_7$Ru, 608.8; found M$^+$, 609. ^{1}H NMR (CDCl$_3$): δ −47.77 (s, 2 H, CH), 2.18 (s, 18 H, C(CH$_3$)$_3$), 2.45 (s, 18 H, C(CH$_3$)$_3$), 2.77 (s, 6 H, CH$_3$), 7.82 (s, 3 H, COCH$_3$). IR (KBr): 1700 cm^{-1} (C:O).

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Table III. Comproportionation Constants (K_c) in Acetonitrile and Dichloromethane Media and Estimated Metal–Metal Distances (d_{M-M}) of the Binuclear Complexes

complex	solvent	log $K_c(1)^a$	log $K_c(2)^b$	d_{M-M}/nm^c
5	CH_3CN	1.3	2.7	1.31
	CH_2Cl_2	1.4	3.9	
Fc-buty-Fc	CH_3CN	1.6		0.95^d
	CH_2Cl_2	1.7^e		

[a] $K_c(1) = [M^{III}-M^{II}]^2/[M^{II}-M^{II}][M^{III}-M^{III}]$. [b] $K_c(2) = [M^{IV}-M^{III}]^2/[M^{III}-M^{III}][M^{IV}-M^{IV}]$. [c] Estimated distances on the basis of X-ray crystal structures of 1,4-bis(4-pyridyl)butadiyne,[26] [Ru(β-diketonato)$_3$],[12] and acetylferrocene.[27] [d] Estimated as the trans configurational structure. [e] From ref 21.

indicate that the two-electron oxidation and reduction of the Ru^{III}–Ru^{III} complex **5** took place in a stepwise manner through the mixed-valence states Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II}, respectively.

The oxidation steps of Fc-buty-Fc were two Nernstian one-electron processes with no following reaction as indicated by the analysis of the triangular-wave voltammograms. The $\Delta E_{1/2}$ value was estimated from the differential pulse voltammetric wave width as above.

Heterobinuclear complex **6** showed two Nernstian one-electron-oxidation steps and a Nernstian one-electron-reduction step on the triangular-wave voltammograms; no following reaction was detected. The reduction step is ascribed to the reduction of Ru^{III} to Ru^{II} because its $E_{1/2}$ value is close to the $E_{1/2}$ value of the cathodic step of **4**. The $E_{1/2}$ value for the first oxidation step of **6** lies near the $E_{1/2}$ values of the oxidation step of Fc-ethy and the first oxidation step of Fc-buty-Fc. It is thus reasonable to assign this step to the oxidation of Fe^{II} to Fe^{III}. Then, the second oxidation step of **6** can be assigned to the oxidation of Ru^{III} to Ru^{IV}.

The equilibrium constants (K_c) for the comproportionation reaction in the binuclear systems are defined as

$$K_c(1) = [M^{III}-M^{II}]^2/[M^{II}-M^{II}][M^{III}-M^{III}]$$

$$K_c(2) = [M^{IV}-M^{III}]^2/[M^{III}-M^{III}][M^{IV}-M^{IV}]$$

$$K_c = \exp[|E_{1/2}(1) - E_{1/2}(2)|F/RT]$$

The calculated comproportionation constants (at 25 °C) of the symmetrical binuclear complexes are presented in Table III together with the estimated metal–metal distance.

The Ru^{III}–Ru^{II} interactions in weakly coupled systems, i.e., $[\{Ru(NH_3)_5\}_2L]^{5+}$ (L = 4,4′-bipyridine type bridging ligand), in aqueous solutions have been extensively studied by Taube and his co-workers.[22-25] Their K_c values are not very much larger than the statistical value of 4, ranging from 6.7 to ca. 26; that of the 4,4′-bipyridine-bridged complex is 20 and varies little with the ionic strength and the solvent. They indicated that "the major factors (apart from the obvious one of electrostatic origin) contributing to the stability of mixed-valence state relative to the isovalent state are an inherent instability of [2,2] state and the inductive effect of the 3+ charge in the mixed-valence state, with stabilization by electron delocalization making only a minor contribution".[23] The electrostatic term arises from the fact that the mutual repulsion energy of the two metal centers in the mixed-valence state is smaller than half the sum of the repulsion energies of the corresponding isovalent states.[24] They estimated these contributions on the basis of an ellipsoid model[23] and the assumption that no electronic contributions are present in the μ-bis(4-pyridyl)methane complex. The results show that the electrostatic contribution is some 25% in most cases. The situation seems more or less similar in our Ru^{III}–Ru^{II} systems: our $K_c(1)$ value for **5** is not very far from the statistical value and is little dependent on the solvent; $^1/_2RT \ln (K_c(1)/4) = 2.0$ kJ mol^{-1} (in CH_3CN) and 2.3 kJ mol^{-1} (in CH_2Cl_2). In our case, the electrostatic contribution may have a larger share owing to the smaller relative permittivities of the solvents, but it is not so large as to overwhelm the balance of contributing factors.

In contrast, $K_c(2)$ for **5** is very large and solvent-dependent: $^1/_2RT \ln (K_c(2)/4) = 6.0$ kJ mol^{-1} (in CH_3CN) and 9.4 kJ mol^{-1} (in CH_2Cl_2). To the authors' knowledge, these values are the largest comproportionation constants ever reported for any spacer type diruthenium complex with a metal–metal distance greater than 1.2 nm. The present data are evidently insufficient, and more extensive studies on wider varieties of such systems are required to elucidate the nature of the interaction between Ru^{IV} and Ru^{III} centers and explain why it is much stronger than that between Ru^{III} and Ru^{II}. Binuclear species based on bis(β-diketonato)ruthenium(III) centers prove quite useful for this purpose because their Ru^{IV}–Ru^{IV} states are experimentally accessible within the potential window of common supporting electrolyte solutions and are stable enough to be examined by means of usual electrochemical techniques.

Acknowledgment. We thankfully acknowledge the experimental assistance given by Mrs. Nakako Tokita and Mr. Akihiro Kawa (Sophia University) and Prof. Haruhiko Tomoda (Shibaura Institute of Technology). We thank Dr. Yasuhiko Yukawa (Niigata University) for the calculations of the metal–metal distances. Our thanks are also due to Prof. F. S. Howell (Sophia University) for correcting the manuscript. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 03303005) from the Ministry of Education, Science and Culture.

Registry No. 1, 128354-91-6; 1^-, 140360-77-6; 1^+, 140360-81-2; 2, 140388-75-6; 2^-, 140388-76-7; 2^+, 140388-77-8; 3, 140360-72-1; 3^-, 140360-78-7; 3^+, 140360-82-3; 4, 140360-73-2; 4^-, 140360-79-8; 4^+, 140360-83-4; 5, 140360-74-3; 5^-, 140360-86-7; 5^{2-}, 140360-89-0; 5^+, 140360-90-3; 5^{2+}, 140360-91-4; 6, 140360-75-4; 6^-, 140360-88-9; 6^+, 140360-87-8; mIma$^-$, 140388-74-5; mESima$^-$, 140360-70-9; mEma$^-$, 140360-71-0; Fe-ethy, 1271-47-2; Fc-buty-Fc, 1273-18-3; Fe-ethy$^+$, 140360-85-6; acac$^-$, 17272-66-1; $PdCl_2(PPh_3)_2$, 13965-03-2; CuI, 7681-65-4; [Ru(mAma)(dpm)$_2$], 140360-76-5; [Ru(mAma)(dpm)$_2$]$^-$, 140360-80-1; [Ru(mAma)(dpm)$_2$]$^+$, 140360-84-5; bis(acetato)copper(II), 142-71-2.

OM910577C

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