A New Synthetic Method for Ruthenium Complexes of β-Diketones from 'Ruthenium Blue Solution' and their Properties*

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(Received February 26, 1988)

Abstract

The 'ruthenium blue solution' obtained by reducing hydrated ruthenium(III) trichloride with ethanol was used as a convenient starting material in the synthesis of thirteen tris(β-diketonato)ruthenium-(III) and six tris(β-diketonato)ruthenate(II) complexes. The procedure of preparing the 'ruthenium blue solution' requires no catalyst and is much simpler than the previous methods. A variety of complexes were synthesized in good yields with small changes of the conditions. The Hammett constants of the substituents on the ligand serve as a helpful guide for choosing the operating conditions for the preparation of β-substituted complexes. The yields of the complexes with β-substituted ligands are relatively small, since the presence of a bulky substituent at the β-position decreases the fraction of the enol form of the free ligand. The melting points, magnetic moments, R_f values in TLC, UV–Vis, IR, and ^1H NMR spectra were measured. The substituent effects on these properties are discussed.

Introduction

The blue product [3] of the catalytic hydrogen reduction of hydrated ruthenium(III) chloride in methanol has been used as a convenient starting material for the synthesis of a number of ruthenium-(III) and ruthenium(II) complexes [4]. Shimizu [5] reported that a blue material was readily obtained by reducing the ruthenium(III) salt with an ethanol–hydrochloric acid mixture and then evaporating the reaction mixture to dryness. He prepared Ru(Hedta)-$(H_2O)\cdot 4H_2O$ by evaporating this material repeatedly with the ligand and portions of hydrochloric acid. The blue product of the ethanol–hydrochloric acid treatment was also used by Endo *et al.* [6, 7] to prepare some tris(β-diketonato)ruthenium(III) complexes. In fact, however, the addition of hydrochloric acid was unnecessary. In its absence, the reduction proceeds more smoothly and the ligand can be added directly to the blue solution.

Previously, the ruthenium complexes with β-diketones were synthesized in different, rather haphazard ways. The complexes $Ru(bhfa)_3$ [7] and $Ru(bhma)_3$ [8] were obtained by heating mixtures of hydrated ruthenium trichloride, potassium hydrogencarbonate, and Hbhfa** or Hbhma (which are solid at room temperature). Similarly, $Ru(fhma)_3$ [8] and K $Ru(fhfa)_3$ [9] were prepared by refluxing a mixture of hydrated ruthenium trichloride, the respective ligand (Hfhma or Hfhfa) and potassium hydrogencarbonate. The complex $Ru(bhba)_3$ [7, 10] was produced through the ligand substitution reaction of $Ru(acac)_3$ in ethyl benzoate. Some other complexes [6, 7] were synthesized by using a blue material obtained by reducing the ruthenium salt with an ethanol–hydrochloric acid mixture and evaporating the reaction mixture to dryness.

The present paper describes a new method for syntheses of tris(β-diketonato)ruthenium(III) and tris(β-diketonato)ruthenate(II) complexes from 'ruthenium blue solution' obtained by ethanolic reduction. Some physical properties of the synthesized complexes were measured.

Experimental

Measurements

A Hitachi Model 200-20 Spectrophotometer was used for recording UV–Vis absorption spectra, and a Hitachi Model 260-50 IR Spectrophotometer was

*For preliminary notes see refs. 1a and 1b. Part of *Doctoral Thesis* of A. Endo [2].

**The following ligand abbreviations will be used in this paper (see Table I): Hfhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hfhoa, 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione; Hbhfa, 4,4,4-trifluoro-1-phenyl-1,3-butanedione; Hfhsa, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; Hfhma,1,1,1-trifluoro-2,4-pentanedione; Hfhpa, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione; Hbhba, 1,3-diphenyl-1,3-propanedione; Hbhma, 1-phenyl-1,3-butanedione; Hacac, 2,4-pentanedione; Hmhpa, 5,5-dimethyl-2,4-hexanedione; Hphpa, 2,2,6,6-tetramethyl-3,5-hexanedione; Hmmma, 3-methyl-2,4-pentanedione; Hmema, 3-ethyl-2,4-pentanedione; HmPrma, 3-isopropyl-2,4-pentanedione; Hmbma, 3-phenyl-2,4-pentanedione.

0020-1693/88/$3.50

used for recording IR spectra. ^{1}H NMR spectra were recorded by a Jeol JMN-FX200 Fourier Transform NMR Spectrometer. GC/MS spectrometry was carried out by means of a Jeol JMS D300 Mass Spectrometer and a Jeol JGL-20K Gas Chromatograph linked with a Jeol JMA-2000 Mass Data Analysis System. Elemental analyses of C and H were carried out by means of a Shimadzu CHN Analyzer CHN-1A. Ruthenium was determined spectrophotometrically according to the ruthenate method [11] after the decomposition of the complexes by concentrated sulfuric acid.

Chemicals

Hydrated ruthenium trichloride was obtained from Nakarai Chemical Ltd. High purity acetonitrile for spectrometry (Dotite Spectrosol) was used for the measurement of UV–Vis spectra. Chromatographic grade benzene and hexane was used throughout all measurements. Deuterized solvents were obtained from C. E. A. France. Merck TLC plates of Kieselgel 60 F_{254} and Alminiumoxid 60 F_{254} (type E) were used for TLC. The β-diketones were obtained as follows: Hfhfa, Hbhfa, Hfhoa, Hfhsa, Hfhma, Hfhpa, Hmbma, Hacac, and Hphpa were purchased from Dojindo Laboratories, Hbhma was from Wako Pure Chemical Industries Ltd. and Hbhba from Tokyo Kasei Ltd. The other β-diketones were synthesized as follows.

Preparation of β-Diketones

5,5-Dimethyl-2,4-hexanedione (Hmhpa) was synthesized according to the method of Iimura [12].

3-Methyl-2,4-pentanedione (Hmmma) was prepared by refluxing a mixture of acetylacetone, methyl iodide, and anhydrous potassium carbonate in acetone according to the literature method [13].

3-Ethyl-2,4-pentanedione (Hmema) was synthesized by refluxing a mixture of acetylacetone and ethyl iodide according to the method used for Hmmma. The crude product was distilled and a fraction at 180 °C was collected. However, GC/MS spectrometry revealed that this fraction was a mixture of 3-ethyl-2,4-pentanedione (*ca.* 90%) and 2,4-heptanedione (*ca.* 10%) (total yield was *ca.* 70%); the latter was produced by the substitution of the hydrogen on a methyl group of acetylacetone. Hmema was separated as the first elution band from a column of Merck Kieselgel 60 reinst (70–230 mesh ASTM). The identification was obtained from its ^{1}H NMR spectrum.

3-Isopropyl-2,4-pentanedione (HmPrma) was also prepared by the method used for Hmmma, except that the refluxing time was *ca.* 30 h. The crude product was vacuum distilled and a fraction at 80 °C (24 mmHg) was collected. Because this fraction was also a mixture of 3-isopropyl-2,4-pentanedione (*ca.* 60%) and 6-methyl-2,4-heptanedione (*ca.* 40%), HmPrma was separated by flash column chromatography with Merck Kieselgel 60 (230–400 mesh ASTM) under nitrogen pressure.

Preparation of 'Ruthenium Blue Solutions'

Hydrated ruthenium trichloride (1 g, or 4.4 mmol as Ru) was dissolved in a mixture of 50 cm^3 of water and 50–100 cm^3 of ethanol. The reddish brown solution was refluxed on a water bath for 4–5 h. The color of the solution turned dark green and then deep blue; a small amount of a black solid (probably ruthenium metal or the oxide) deposited on the wall of the glass vessel. Too long refluxing brought about a large amount of the deposit. This solution was very sensitive to air.

The fraction of water in the original mixture of water and ethanol can be varied; in the absence of any water, the reaction stopped at the stage of the green solution.

Preparation of the Complexes

The general procedure is as follows. An excess amount of ligand is introduced quickly into the 'ruthenium blue solution' (4.4 mmol as Ru), and the mixture is refluxed until its color turned red (about 30 min to 2–3 h, depending on the kind of the ligand). The mixture is cooled, and a portion of potassium hydrogencarbonate is added in order to neutralize the liberated hydrogen ions; then the mixture is refluxed again for 1–2 h. This procedure is repeated. The color of the mixture gradually turns blue or purple except in the cases of **7** and **9**–**14** (Table I). After the addition of the last portion of the carbonate, refluxing is continued for 1–3 h. Up to this point, air should be excluded as far as possible. Then the solution is concentrated to *ca.* 50 cm^3 in a rotary evaporator. The precipitate is collected by filtration and is dried under a vacuum. The precipitate is extracted with *ca.* 20 cm^3 portions of benzene. The deep red benzene extract, which contains the ruthenium(III) species, is passed through a column of Merck Alminiumoxid 90 (aktivitätsstufe II-III), and the column is washed with benzene. The eluent is concentrated to dryness. Each residue is recrystallized from ethanol except for [Ru(bhba)$_3$], which is recrystallized from benzene–ethanol (1 to 1 by volume). When the ruthenium(II) species is stable in air, as in the cases of the complexes possessing trifluoromethyl substituents, it is obtained by extracting the residue of the benzene extraction with acetone. The acetone extract is passed through a column of Merck Kiesel Gel 60. The eluent is evaporated to dryness. The crystals are washed with benzene and dried under a vacuum.

In the above procedure, the amount-of-substance ratio of ligand to ruthenium, the amount-of-substance ratio of $KHCO_3$ to ligand, and the number of fractions of $KHCO_3$ were changed as shown in Table I.

TABLE I. Conditions for the Synthesis and Yields of $[Ru^{III}L_3]$ and $K[Ru^{II}L_3]$ (L = RCOCR'COR'')

	Complex	R	R'	R''	Color of the crystal	R_{ligand}[a]	R_{alkali}[b]	n[c]	Yield (%)[d]	$\Sigma\sigma_{p,m}$
1	$[Ru(fhfa)_3]$	CF_3	H	CF_3	dark red	3.3	1.5	2	0	+2.34
1'	$K[Ru(fhfa)_3]$				purple				56	
2	$[Ru(fhoa)_3]$	CF_3	H	C_4H_3O	brownish red	3.3	1.5	2	41	+1.89
2'	$K[Ru(fhoa)_3]$				blue					
3	$[Ru(bhfa)_3]$	CF_3	H	C_6H_5	dark red	3.3	1.5	1	29	+1.59
3'	$K[Ru(bhfa)_3]$				blue				55	
4	$[Ru(fhsa)_3]$	CF_3	H	C_4H_3S	brownish red	3.3	1.5	2	56	+1.59
4'	$K[Ru(fhsa)_3]$				blue					
5	$[Ru(fhma)_3]$	CF_3	H	CH_3	dark red	3.3	1.5	2	6	+1.11
5'	$K[Ru(fhma)_3]$				purple				58	
6	$[Ru(fhpa)_3]$	CF_3	H	$C(CH_3)_3$	red	3.3	1.5	2	12	+1.02
6'	$K[Ru(fhpa)_3]$				purple				40	
7	$[Ru(bhba)_3]$	C_6H_5	H	C_6H_5	black	3.3	1.5	2	47	−0.06
8	$[Ru(bhma)_3]$	C_6H_5	H	CH_3	dark red	3.3	1.5	2	78	−0.54
9	$[Ru(mbma)_3]$	CH_3	C_6H_5	CH_3	dark red	3.3	1.0	2	33	−0.84
10	$[Ru(acac)_3]$	CH_3	H	CH_3	dark red	3.3	1.0	2	70	−1.02
11	$[Ru(mhpa)_3]$	CH_3	H	$C(CH_3)_3$	orange–red	4.5	0.7	3	8	−1.11
12	$[Ru(phpa)_3]$	$C(CH_3)_3$	H	$C(CH_3)_3$	orange	4.5	0.7	3	30	−1.20
13	$[Ru(mmma)_3]$	CH_3	CH_3	CH_3	dark red	4.5	0.7	3	11	−1.23
14	$[Ru(mema)_3]$	CH_3	C_2H_5	CH_3	dark red	4.5	0.7	3	12	−1.23
	$[Ru(mPrma)_3]$	CH_3	$CH(CH_3)_2$	CH_3		4.5	0.7	3	0	−1.23

[a] R_{ligand} = amount-of-substance ratio of ligand to Ru; Ru = 4.4 mmol. [b] R_{alkali} = amount-of-substance ratio of $KHCO_3$ to ligand. [c] Number of fractions of $KHCO_3$. [d] The yield is calculated on the basis of the amount-of-substance of ruthenium.

The ruthenium(II) complexes listed in Table I, except $K[Ru(fhfa)_3]$ and $K[Ru(fhma)_3]$, are new compounds. (*Anal.* $K[Ru(fhoa)_3]$, Found: C, 40.5; H, 1.5; Ru, 15.2. Calc. for $K[RuC_{24}H_{12}F_9O_9]$: C, 38.2; H, 1.6; Ru, 13.4%. $K[Ru(bhfa)_3]$, Found: C, 46.4; H, 2.3. Calc. for $K[RuC_{30}H_{21}F_9O_6]$: C, 45.9; H, 2.3%. $K[Ru(fhsa)_3]$, Found: C, 36.3; H, 1.9; Ru, 12.4. Calc. for $K[RuC_{24}H_{12}F_9O_6S_3]$: C, 35.9; H, 1.5; Ru, 12.6%. $K[Ru(fhpa)_3]$, Found: C, 39.5; H, 4.2; Ru, 13.3%. Calc. for $K[RuC_{24}H_{30}F_9O_6]$: C, 39.7; H, 4.2; Ru, 13.9%.) They are readily soluble in acetonitrile, acetone and ethanol giving blue (**2'–4'**) or purple (**6'**) solutions, but they are sparingly soluble in benzene and water. These crystals are fairly stable in air and can be kept for several days, but storage under nitrogen or argon is recommended. They are readily converted to the corresponding ruthenium(III) species with hydrogen peroxide. For example, $[Ru^{III}(fhfa)_3]$, which could not be produced at all by the method described above, was obtained by oxidizing $K[Ru^{II}(fhfa)_3]$ as follows. The potassium salt (1.6 g) was suspended in 100 cm^3 of water. Then, 100 cm^3 of benzene was added to the suspended solution. The solution with 1 cm^3 of *ca.* 4 mol dm^{-3} HCl solution was also added and an aqueous solution of hydrogen peroxide (mass fraction = 1%) was added dropwise to the mixture, which was stirred. The oxidized complex was extracted into benzene. The benzene phase was separated and was evaporated to dryness. The residue was again extracted with hexane. The extract was evaporated to dryness, and the crystals were dried under a vacuum. The crystals are not very stable even under nitrogen atmosphere in the absence of light. The yield was 62% on the basis of $K[Ru(fhfa)_3]$.

When only the ruthenium(III) complexes, with the exception $[Ru(fhfa)_3]$, are to be prepared, hydrogen peroxide may be added dropwise after the last refluxing until the color of the solution returns to red.

Among the ruthenium(III) complexes in Table I, $[Ru(fhoa)_3]$ (**2**), $[Ru(fhpa)_3]$ (**6**), $[Ru(mhpa)_3]$ (**11**), $[Ru(mmma)_3]$ (**13**), $[Ru(mema)_3]$ (**14**) are new compounds. (*Anal.* $[Ru(fhoa)_3]$, Found: C, 42.0; H, 1.7. Calc. for $[RuC_{24}H_{12}F_9O_9]$: C, 40.2; H, 1.7%. $[Ru(fhpa)_3]$, Found: C, 42.1; H, 4.5. Calc. for $[RuC_{24}H_{30}F_9O_6]$: C, 42.0; H, 4.4%. $[Ru(mhpa)_3]$, Found: C, 63.0; H, 5.3; Ru, 16.3. Calc. for $[RuC_{24}H_{39}O_6]$: C, 63.2; H, 5.3; Ru, 16.1%. $[Ru(mmma)_3]$: C, 48.7; H, 6.1; Ru, 23.6. Calc. for $[RuC_{18}H_{27}O_6]$: C, 49.1; H, 6.2; Ru, 22.9%. $[Ru(mema)_3]$, Found: C, 52.1; H, 7.0; Ru, 21.2. Calc. for $[RuC_{21}H_{33}O_6]$: C, 52.3; H, 6.9; Ru, 20.9%.)

They are readily soluble in benzene, carbontetrachloride, acetonitrile, and acetone giving red solutions; but they are sparingly soluble in water.

In the case of the syntheses of $[Ru(mmma)_3]$ and $[Ru(mema)_3]$, a red by-product was formed. So, these two complexes were isolated by column chromatography with Alminiumoxid and benzene.

Results and Discussion

Ruthenium Blue Solution

Rose and Wilkinson [3, 4] reported that a blue solution obtained by the catalytic hydrogen reduction of hydrated ruthenium(III) chloride contained the species $Ru_5Cl_{12}^-$. The electrolytic reduction of the K_2RuCl_5 in an acidic solution gave another kind of blue species, which was identified as a mixture of dimeric ruthenium(II, III) species of the type $Ru_2Cl_{3+n}^{(2-n)+}$ ($n = 0, 1, 2$) (see 'Experimental') [14]. Bino and Cotton [15] obtained a different kind of blue solution by dissolving $Ru(O_2CCH_3)_4Cl$ in 12 mol dm^{-3} HCl solution; this complex was identified as a trinuclear, mixed-valence chloro complex, $Ru_3Cl_{12}^{4-}$ [15].

Since the blue species so far identified are all mixed-valence chloro complexes, the blue species contained in the present 'ruthenium blue solution' was thought likely to be similar. But its spectrum was not consistent with any of the above-mentioned species, and the attempt to identify it was not successful.

The present procedure of preparing the 'ruthenium blue solution' by the ethanolic reduction is very simple in comparison with the previous methods. Furthermore, a specific catalyst is unnecessary; and β-diketonato complexes and many other complexes can be synthesized simply by adding the ligand directly to the 'ruthenium blue solution'.

Yields

In Table I, the complexes are numbered in decreasing order (from positive to negative) of the sum of the Hammett constants [16] of the substituents on the ligands: $\Sigma\sigma_{p,m} = 3(\sigma_p(R) + \sigma_m(R') + \sigma_p(R''))$, where $\sigma_p(R)$ and $\sigma_p(R'')$ are Hammett constants for the *para* substituent R and R'', respectively, and $\sigma_m(R')$ is Hammett constant for the *meta* substituent R'. Since a larger positive value of $\Sigma\sigma_{p,m}$ means a stronger electron-withdrawing power of the substituents, it is expected that the ruthenium(II) state will become more relatively stable with respect to the ruthenium(III) state when this value is more positive. Indeed, the complexes of **1'–6'**, which have more positive $\Sigma\sigma_{p,m}$ than the others, can be isolated, and are fairly stable in air; in the case of $[Ru(bhma)_3]$ which has a less positive value of $\Sigma\sigma_{p,m}$ than **1'–6'**, the ruthenium(II) species were present in the reaction mixture, but they were oxidized when exposed to air during the subsequent handling. It is inferred that tris(β-diketonato)ruthenate(II) complexes can be obtained quite easily when $\Sigma\sigma_{p,m}$ is larger than *ca.* +1.0.

The ratio of the yield of the ruthenium(III) complex to that of the ruthenium(II) complex varied appreciably from run to run, while the total yield was almost constant.

Interestingly, the order in Table I is roughly parallel to that of the relative ease of preparation as seen in the yields and as suggested by the conditions for the preparation in Table I. The smaller $\Sigma\sigma_{p,m}$ is, the less easy the complex formation becomes. In the synthesis of a complex having a negative $\Sigma\sigma_{p,m}$ value, the addition of a large excess of the ligand, milder conditions for the neutralization, and long refluxing time will be preferable, especially in the cases of **11–14**. On the contrary, the complexes possessing a large positive $\Sigma\sigma_{p,m}$ can be synthesized in good yields without careful control of the conditions. This fact can be attributed to the effect of the electron-withdrawing substituent on the acid dissociation constant (K_a) of the ligand: e.g. $pK_a = 6.0$ for Hfhfa, 14.2 for Hmhpa in 75% dioxane–H_2O at 30 °C [17].

The yields for the γ-substituted complexes appear to be affected not only by the electron-withdrawing power but also by the steric effect of the γ-substituent. The yield of $[Ru(mbma)_3]$ was only about a half that of $[Ru(acac)_3]$ although the $\Sigma\sigma_{p,m}$ value is more positive for the former than the latter; the yields of $[Ru(mema)_3]$, $[Ru(mmma)_3]$ and $[Ru(mPrma)_3]$ were very much lower than that of $[Ru(phpa)_3]$, while their $\Sigma\sigma_{p,m}$ values are nearly the same. The presence of a bulky substituent at the γ-position lowers the fraction of the enol form in the keto–enol equilibrium of the free ligand [18]. The fraction of the enol form is *ca.* 30% for Hmmma, *ca.* 26% for Hmema, and *ca.* 0% for HmPrma [19], whereas the fraction of enol form is *ca.* 80% for Hacac. The fraction of the enol form in the keto–enol equilibrium is a very important factor in the synthesis of the ruthenium complexes with β-diketone, because the ligand must take the enolate form before it coordinates.

Accordingly, by this method, it will be impossible to synthesize the ruthenium complexes of acetylacetone derivatives with such γ-substituents as $-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$, $-C(CH_3)_3$, for which the equilibrium fraction of the enol form is expected to be quite low – practically zero.

The complexes with unsymmetrical ligands have geometrical isomers, facial and meridional. In fact, the ^1H NMR spectra revealed that a mixture of the two isomers was obtained for $[Ru(fhoa)_3]$, $[Ru(bhfa)_3]$, $[Ru(fhma)_3]$, $[Ru(fhpa)_3]$, and $[Ru(bhma)_3]$. But, in the cases of $[Ru(fhsa)_3]$ and $[Ru(mhpa)_3$, only the meridional isomers were prepared.

TABLE II. Thermal and Magnetic Properties and Wave Numbers of the C---O and C---C Stretching of the Tris(β-diketonato)-ruthenium(III) and -ruthenate(II) Complexes

Complex		t (°C)[a]	μ_{eff}/μ_B[b]	$\tilde{\nu}$(C---O) (cm^{-1})	$\tilde{\nu}$(C---C) (cm^{-1})
1	$[Ru(fhfa)_3]$	*ca.* 85(s)	1.90	1585	1580
2	$[Ru(fhoa)_3]$[c]	*ca.* 164(s)	1.87	1570	1560
3	$[Ru(bhfa)_3]$[c]	*ca.* 190(s)	1.84	1565	1540
4	$[Ru(fhsa)_3]$[d]	174–176(m)	1.75	1560	1530
5	$[Ru(fhma)_3]$[c]	*ca.* 138(s)	1.92	1590	1515
6	$[Ru(fhpa)_3]$[c]	85–87(m)	1.84	1560	1500
7	$[Ru(bhba)_3]$	*ca.* 270(d)	1.92	1510	1470
8	$[Ru(bhma)_3]$[c]	219–222(m)	2.18	1530	1510
9	$[Ru(mbma)_3]$	*ca.* 220(d)	1.79	1550	1420
10	$[Ru(acac)_3]$	*ca.* 180(s)	1.90	1530	1510
11	$[Ru(mhpa)_3]$[d]	92–94(m)	1.91	1540	1510
12	$[Ru(phpa)_3]$	*ca.* 137(s)	1.84	1530	1500
13	$[Ru(mmma)_3]$	*ca.* 175(s)	1.84	1555	1480
14	$[Ru(mema)_3]$	*ca.* 155(s)	1.84	1545	1450
1′	$K[Ru(fhfa)_3]$		0.63	1560	1530
2′	$K[Ru(fhoa)_3]$[c]		0.44	1570	1510
3′	$K[Ru(bhfa)_3]$[c]		0.40	1560	1520
4′	$K[Ru(fhsa)_3]$[d]		1.04	1620	1505
5′	$K[Ru(fhma)_3]$[c]		0.45	1575	1505
6′	$K[Ru(fhpa)_3]$[c]		0.44	1570	1490

[a] m, s, and d denote melting, sublimation, and decomposition, respectively. [b] μ_{eff} denotes effective magnetic moment, and μ_B Bohr Magneton, respectively. [c] The mixture of facial and meridional isomers. [d] Meridional isomer.

Melting Point

The melting points of the ruthenium(III) complexes are shown in Table II. Most of the complexes sublimed, but the starting temperatures of the sublimation were not clear. Generally, the substitution of fluorine for hydrogen in the β-diketonato ligands is known to increase greatly the volatility of the complex, and inversely, the substitution of phenyl, furyl, or thienyl groups for a methyl group is known to decrease the volatility of the complex [18]. In the present case, too, the $[Ru(fhfa)_3]$ sublimed at a very low temperature and none of the complexes having phenyl substituents showed noticeable volatility.

The ruthenium(II) complexes seem to decompose and/or to oxidize gradually to the corresponding ruthenium(III) complexes, which then may sublime at *ca.* 200 °C or a higher temperature.

Magnetic Properties

The effective magnetic moments of the ruthenium(III) and the ruthenium(II) complexes obtained by the Faraday method or the Gouy method are shown in Table II. These values are corrected for diamagnetism of the ligands calculated by the value of each atom [20]. The values of μ_{eff} of the ruthenium(III) complexes indicate the presence of one unpaired electron. Since the Ru^{III} have d^5 electronic configuration, the ruthenium(III) complexes must have the low spin electronic configuration. The electronic configuration of the ruthenium(II) complexes also must be low spin, as shown by their small μ_{eff} values.

Grobelny *et al.* [20] examined the magnetic properties of $[Ru(acac)_3]$, $[Ru(bhma)_3]$, and $[Ru(bhba)_3]$. Their μ_{eff}/μ_B values (1.66 for $[Ru(acac)_3]$, 1.81 for $[Ru(bhma)_3]$, 1.65 for $[Ru(bhba)_3]$) are slightly smaller than the values in Table II.

IR Spectra

The IR spectra of many metal acetylacetonato complexes show very strong, characteristic absorption peaks corresponding to the C---O stretching mode around 1570 cm^{-1} [18, 21–24]. The C---O and C---C stretching bands of the ruthenium(II) and ruthenium(III) β-diketonato complexes appear in the 1510–1620 cm^{-1} and the 1420–1580 cm^{-1} regions depending on the substituents (Table II). For the complexes having trifluoromethyl substituents, the frequencies of both absorption peaks were higher than for the others. Such shifts were explained in terms of the strong electron-withdrawing power of the trifluoromethyl group, and the consequent strengthening of the C---O and C---C bonding [18, 21]. There seems to be no clear relationship between the C---O and C---C stretching frequencies of β-substituted complexes and the sum of the Hammett constants of the substituents, although a linear

TABLE III. The Wavelength of the Absorption Maxima and Molar Absorption Coefficients of UV–Vis Spectra in Acetonitrile at Room Temperature

		λ_{max} (nm) ($\log(\epsilon/mol^{-1}\ dm^3\ cm^{-1})$)	
		Complex	Ligand
1	$[Ru(fhfa)_3]$	531(3.27), 374(3.94), 285(4.09)	272(–)
2	$[Ru(fhoa)_3]$[a]	564(sh), 406(4.47), 330(4.75), 239(4.09)	364(4.13), 321(4.14), 273(sh), 235(sh)
3	$[Ru(bhfa)_3]$[a]	565(sh), 410(4.36), 333(4.71), 274(4.20)	327(4.15), 300(sh), 260(sh), 224(3.53)
4	$[Ru(fhsa)_3]$[b]	550(sh), 396(4.24), 306(4.65), 265(sh)	353(sh), 325(4.08), 272(sh)
5	$[Ru(fhma)_3]$[a]	518(3.15), 360(3.93), 276(4.15)	286(–)
6	$[Ru(fhpa)_3]$[a]	518(3.14), 365(3.94), 278(4.19)	288(–)
7	$[Ru(bhba)_3]$	570(sh), 430(4.14), 331(4.72), 295(sh), 258(4.60)	341(4.33), 250(3.95)
8	$[Ru(bhma)_3]$[a]	530(sh), 396(4.05), 300(4.55), 247(4.44)	307(4.11), 246(3.82)
9	$[Ru(mbma)_3]$	523(3.43), 370(4.01), 280(sh), 272(4.17)	285(3.94), 224(sh)
10	$[Ru(acac)_3]$	506(3.19), 349(3.94), 272(4.24)	272(–)
11	$[Ru(mhpa)_3]$[b]	502(3.18), 355(3.87), 277(4.22)	–
12	$[Ru(phpa)_3]$	496(3.24), 368(3.88), 279(4.25)	276(–)
13	$[Ru(mmma)_3]$	545(3.30), 366(3.98), 285(4.12)	289(–)
14	$[Ru(mema)_3]$	539(3.32), 373(3.96), 288(4.11)	290(–)
1′	$K[Ru(fhfa)_3]$	529(4.22), 494(sh), 288(4.31), 234(3.98)	
2′	$K[Ru(fhoa)_3]$[a]	599(4.36), 550(sh), 315(4.62), 302(sh), 283(sh)	
3′	$K[Ru(bhfa)_3]$[a]	591(4.38), 450(sh), 296(4.69), 255(4.41)	
4′	$K[Ru(fhsa)_3]$[b]	612(4.35), 570(sh), 314(4.71), 262(4.28)	
5′	$K[Ru(fhma)_3]$[a]	525(4.08), 490(sh), 280(4.37), 245(sh)	
6′	$K[Ru(fhpa)_3]$[a]	530(4.17), 490(sh), 281(4.37), 242(4.09)	

[a] The mixture of facial and meridional isomers. There was a small difference of λ_{max} and ϵ between facial and meridional. [b] Meridional isomers.

correlation is reported in the case of a series of β-substituted tris(β-diketonato)cobalt(III) complexes [25].

The substitution at the γ-position increases the C===O stretching frequency and decreases the C===C stretching frequency. In the case of bis(β-diketonato)-copper(II) complexes, the replacement of the hydrogen at the γ-position by substituents with increasing relative masses makes the C===O frequency lower [21]. On the contrary, the C===O stretching frequencies of **9**, **13**, and **14** are higher than that of $[Ru(acac)_3]$.

UV–Vis Spectra

In acetonitrile solutions, the ruthenium(III) complexes with aliphatic substituents, for example, $[Ru(acac)_3]$ and $[Ru(phpa)_3]$, showed three absorption peaks. Those with aromatic substituents showed one or two additional peaks and shoulders, which are attributable to the adsorption of the aromatic substituents themselves. The wavelengths of the absorption peaks and shoulders of the ruthenium(III) complexes and their molar absorption coefficients are presented in Table III, together with those of the free ligands.

Grobelny *et al.* [20] have made a tentative assignment of the absorption bands of $[Ru(acac)_3]$ and $[Ru(bhma)_3]$ in ethanol and $[Ru(bhba)_3]$ in dioxane (these spectra are exactly the same as those in acetonitrile solutions). Recently, Satsu *et al.* [26] have assigned accurately the three absorption bands of $[Ru(acac)_3]$: they ascribed the absorption bands to the transition to the excited states that are the configuration–interaction admixtures of the ligand (π, π^*) excited triplet states, the ligand-to-metal charge-transfer (LMCT) exited states, and the ligand (π, π^*) singlet states.

The spectra of all the ruthenium(II) complexes are similar to each other whether the aromatic or aliphatic substituents are present or not, in contradistinction to the cases of the ruthenium(III) complexes.

^1H NMR Spectra

Two typical ^1H NMR spectra are shown in Fig. 1a and b. The spectrum of $[Ru(phpa)_3]$, which has D_3 symmetry, is very simple; it consists of two peaks corresponding to the absorption of the t-butyl protons and methyne protons of the ligands. The sample of $[Ru(fhma)_3]$ showed eight peaks, corresponding to the methyl protons and methyne protons of the ligands. These peaks arise from the presence of the two geometrical isomers, facial and meridional. Since *fac*-$[Ru(fhma)_3]$ has C_3 symmetry, the three methyl groups of the ligands are equivalent

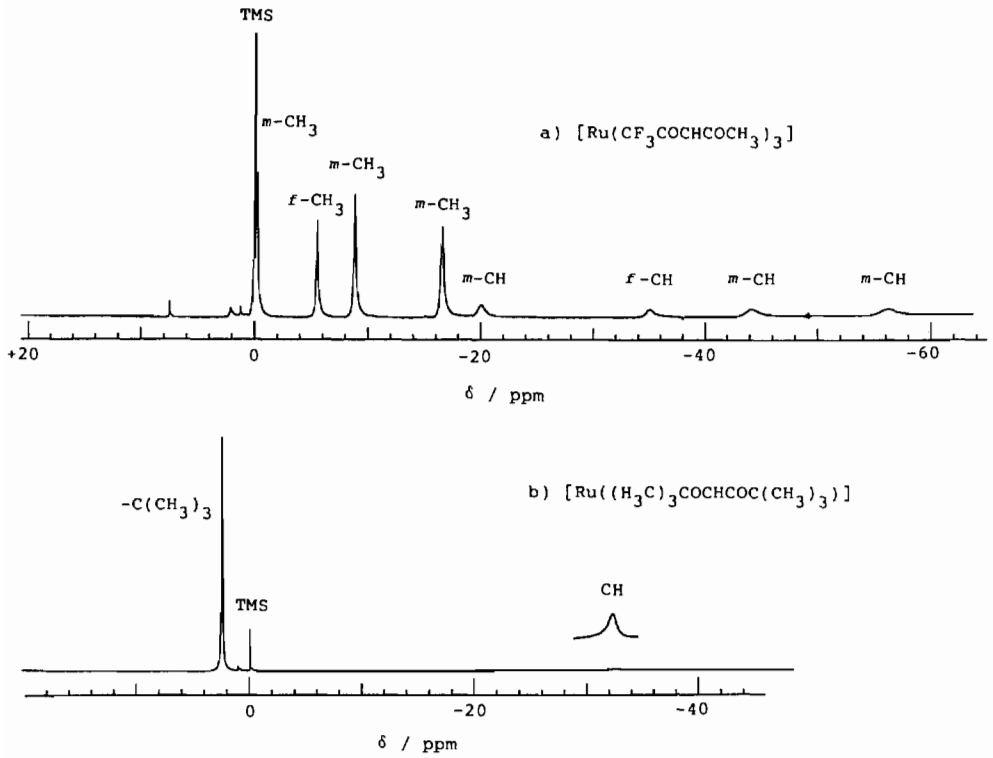

Fig. 1. Typical ^1H NMR spectra.

and so are the three methyne protons. Hence, *fac*-[Ru(fhma)$_3$] gives two peaks. On the other hand, *mer*-[Ru(fhma)$_3$] has C_1 symmetry in which neither the three methyl groups nor the three methyne protons are equivalent, and this isomer gives six peaks. The proton chemical shifts of the ruthenium(III) complexes are shown in Table IV. For [Ru(bhfa)$_3$] (**3**) [27], [Ru(fhma)$_3$] (**5**) and [Ru(fhpa)$_3$] (**6**) the samples were isolated as facial and meridional isomers. The signals of the methyne protons of all the ruthenium(III) complexes appear at very high field region because of the paramagnetism of the ruthenium(III) complexes. The position of the signal of the methyne protons would be lowered by electron-withdrawing substituents, if the complex were diamagnetic [18]. However, the signals of the methyne protons of [Ru(fhfa)$_3$] (**1**) and [Ru(bhba)$_3$] (7) shifted to more upfield than that of [Ru(acac)$_3$] (**10**), in spite of the presence of more electron-withdrawing substituents. The methyne signal of [Ru(phpa)$_3$] (**12**) is again more upfield than that of [Ru(acac)$_3$]. No simple explanation has been found yet.

All the proton signals of the ruthenium(II) complexes are found between 0 and 10 ppm. Their assignment was possible only for K[Ru(fhfa)$_3$] (**1'**) and K[Ru(fhma)$_3$] (**5'**) (Table IV), because the expected signals appeared separately. For the other ruthenium(II) complexes, the assignment was rendered impossible by the presence of too many signals squeezed into a narrow region (for **3'** and **4'**) or by the presence of fewer signals than expected (**2'** and **6'**).

Thin Layer Chromatography

A variety of solvents and substrates have been used for the thin-layer chromatographic separation of acetylacetonato complexes [28, 29] and the separation of β-diketonates of iron(III), cobalt(III) and chromium(III) has been investigated by using several aprotic solvents [30].

So far thin-layer chromatography has been widely used for the separation of geometrical and/or optical isomers of ruthenium complexes with unsymmetrical ligands [8, 27, 32, 32]. The geometrical isomers of [Ru(fhma)$_3$] and [Ru(bhma)$_3$] were separated on a column of activated silica gel (for [Ru(fhma)$_3$]) or acid-washed alumina (for [Ru(bhma)$_3$]) with benzene–hexane mixture (1 to 1 by volume) as developing solvent (for both complexes) [8]. The geometrical isomers of [Ru(bhfa)$_3$] and [Ru(bhfa)$_2$(acac)] were also separated on a silica gel column with benzene–hexane (12 to 7 by volume) [28]. The geometrical and optical isomers of tris((+)-3-acetylcamphorato)ruthenium(III) complexes were separated on preparative layer silica gel plates with a mixture of heptane–ethyl ether (1 to 1 by volume)) [32]. The separation of the optical isomers of

TABLE IV. Chemical Shifts (δ) of ^1H NMR Spectra of $[Ru(RCOCR'COR'')_3]$ (in $CDCl_3$) and $K[Ru(RCOR'COR'')_3]$ (in $(CD_3)_2CO$) Referred to the Signal of TMS at Room Temperature

	$[Ru(RCOCR'COCR'')_3]$	δ (ppm)[a]		
		R	R''	R'
1	$[Ru(CF_3COCHCOCF_3)_3]$			−43.2
2	$[Ru(CF_3COCHCOC_4H_3O)_3]$		*mer* + *fac*: 5.7, 5.9, 6.4, 6.6, 6.7, 7.3, 7.4 7.9, 8.8, 9.5, 10.1, 12.0, 12.3, 13.4	*mer*: −23.1, −44.3, −50.9 *fac*: −35.3
3	$[Ru(CF_3COCHCOC_6H_5)_3]$		*mer:* 6.0, 6.3, 7.2, 8.4, 9.0, 9.5, 10.9, 11.5 *fac*: 6.9, 9.0, 11.7	*mer*: −21.7, −41.5, −49.7 *fac*: −35.5
4	$[Ru(CF_3COCHCOC_4H_3S)_3]$		*mer*: 5.2, 5.5, 6.5, 7.3, 7.5, 8.4, 9.0, 10.5, 10.6	*mer*: −23.9, −43.4, −49.3
5	$[Ru(CF_3COCHCOCH_3)_3]$		*mer*: −0.1, −9.0, −16.9 *fac*: −5.6	*mer*: −20.1, −44.7, −57.0 *fac*: −35.4
6	$[Ru(CF_3COCHCOC(CH_3)_3)_3]$		*mer*: −1.16, −1.27, −2.79 *fac*: −2.79	*mer*: −27.8, −40.0, −49.4 *fac*: −36.3
7	$[Ru(C_6H_5COCHCOC_6H_5)_3]$	11.8, 9.2, 6.72, 6.69	= R	−32.9
8	$[Ru(C_6H_5COCHCH_3)_3]$	*mer* + *fac*: 6.4, 6.70, 6.74, 6.9, 8.7, 8.9, 9.0, 9.5, 11.5, 11.8	*mer* + *fac*: −3.2, −5.7, −6.8, −11.3	*mer*: −24.3, −31.5, −41.6 *fac*: −31.5
9	$[Ru(CH_3COC(C_6H_5)COCH_3)_3]$	−9.6	= R	4.8, 6.6, 9.6
10	$[Ru(CH_3COCHCOCH_3)_3]$	−5.5	= R	−29.9
11	$[Ru(CH_3COCHCOC(CH_3)_3)_3]$	*mer*: −1.5, −3.5, −16.6	*mer*: 1.3, 3.2, 3.4	*mer*: −25.6, −26.4, −48.6
12	$[Ru((CH_3)_3CCOCHCOC(CH_3)_3)_3]$	2.5	= R	−32.8
13	$[Ru(CH_3COC(CH_3)COCH_3)_3]$	−9.3	= R	−34.2
14	$[Ru(CH_3COC(C_2H_5)COCH_3)_3]$	−10.0	= R	2.2, 28.0, 29.2
1′	$K[Ru(CF_3COCHCOCF_3)_3]$			6.2
2′	$K[Ru(CF_3COCHCOC_4H_3O)_3]$		*mer* + *fac*: 2.8, 6.5, 7.3, 7.8, 8.5	
3′	$K[Ru(CF_3COCHCOC_6H_5)_3]$		*mer* + *fac*: 3.0, 7.18, 7.29, 7.33, 7.37, 7.61, 7.64, 7.70, 8.28, 8.32, 8.5	
4′	$K[Ru(CF_3COCHCOC_4H_3S)_3]$		*mer*: 2.8, 4.0, 4.2, 4.9, 6.9, 7.0, 7.66, 7.77, 7.83	
5′	$K[Ru(CF_3COCHCOCH_3)_3]$		*mer*: 1.82, 1.86, 1.93 *fac*: 3.0	*mer*: 5.4, 5.5, 5.7 *fac*: 7.4
6′	$K[Ru(CF_3COCHCOC(CH_3)_3)_3]$		*mer*: 1.07, 1.14 *fac*: 2.8	*mer*: 5.7[b] *fac*: 7.3

[a] *fac* and *mer* denote facial and meridional isomers, respectively. [b] Very broad peak.

TABLE V. R_f Values of Tris(β-diketonato)ruthenium(III) Complexes[a] at Room Temperature

Complex		R_f					
		Benzene		Benz–Hex (3:2)[b]		Benz–Hex (2:3)[c]	
		alumina	silica gel	alumina	silica gel	alumina	silica gel
1	$[Ru(fhfa)_3]$						
2	$[Ru(fhoa)_3]$	*fac* 0.90 *mer* 0.94	*fac* 0.76 *mer* 0.88	*fac* 0.68 *mer* 0.77	*fac* 0.30 *mer* 0.50	*fac* 0.38 *mer* 0.50	*fac* 0.09 *mer* 0.18
3	$[Ru(bhfa)_3]$	0.98	0.97	*fac* 0.89 *mer* 0.94	*fac* 0.83 *mer* 0.88	*fac* 0.73 *mer* 0.81	*fac* 0.49 *mer* 0.60
4	$[Ru(fhsa)_3]$	*mer* 0.96	*mer* 0.94	*mer* 0.82	*mer* 0.66	*mer* 0.55	*mer* 0.25
5	$[Ru(fhma)_3]$	*fac* 0.93 *mer* 0.96	*fac* 0.85 *mer* 0.92	*fac* 0.80 *mer* 0.82	*fac* 0.47 *mer* 0.65	*fac* 0.59 *mer* 0.67	*fac* 0.21 *mer* 0.33
6	$[Ru(fhpa)_3]$	0.98	0.97	*fac* 0.90 *mer* 0.98	*fac* 0.94 *mer* 0.96	*fac* 0.90 *mer* 0.96	*fac* 0.94 *mer* 0.89
7	$[Ru(bhba)_3]$	0.96	0.87	0.64	0.24	0.29	0.05
8	$[Ru(bhma)_3]$	*fac* 0.57 *mer* 0.69	*fac* 0.11 *mer* 0.22	*fac* 0.14 *mer* 0.20	0.04	0.07	0.01
9	$[Ru(mbma)_3]$	0.65	0.16	0.23	0.04	0.09	0
10	$[Ru(acac)_3]$	0.34	0.06	0.10	0.02	0.03	0
11	$[Ru(mhpa)_3]$	*mer* 0.76	*mer* 0.30	*mer* 0.51	*mer* 0.10	*mer* 0.26	*mer* 0.04
12	$[Ru(phpa)_3]$	0.98	0.97	0.98	0.94	0.95	0.83
13	$[Ru(mmma)_3]$	0.42	0.06	0.13	0.03	0.05	0
14	$[Ru(mema)_3]$	0.46	0.06	0.15	0.02	0.05	0

[a] *fac* and *mer* denote facial and meridional isomers, respectively. [b] Mixture of benzene(3)–hexane(2) by volume. [c] Mixture of benzene(2)–hexane(3) by volume.

TABLE VI. R_f Values of Tris(β-diketonato)ruthenate(II) Complexes[a] on Silica Gel at Room Temperature

	Complex	R_f	
		Ethanol	Benzene–Acetone (1:1 by volume)
1′	$K[Ru(fhfa)_3]$	0.81	0.54
2′	$K[Ru(fhoa)_3]$	≃0	≃0
3′	$K[Ru(bhfa)_3]$	0.81	*fac* 0.55, *mer* 0.70
4′	$K[Ru(fhsa)_3]$	0.83	0.49
5′	$K[Ru(fhma)_3]$	0.83	*fac* 0.72, *mer* 0.79
6′	$K[Ru(fhpa)_3]$	0.87	*fac* 0.81, *mer* 0.94

[a] *fac* and *mer* denote meridional and facial isomers, respectively.

$[Ru(acac)_3]$, $[Ru(phpa)_3]$ and $[Ru(fhfa)_3]$ was carried out on a stationary chiral phase packed column (only $[Ru(acac)_3]$ was completely resolved) [33].

The separation of the seventeen tris(β-diketonato)-ruthenium(III) complexes shown in Table V by means of thin-layer chromatography on silica gel and alumina was examined by using benzene, benzene–hexane mixtures (3 to 2 and 2 to 3 by volume) and ethanol. The R_f values of the complexes are summarized in Table V. Among, them, $[Ru(fhfa)_3]$ was not developed, because this complex was reduced to the ruthenium(II) complex both on silica gel and on alumina. The R_f values of the complexes having trifluoromethyl and t-butyl substituents were larger than those of the others. The geometrical isomers of $[Ru(fhoa)_3]$, $[Ru(bhfa)_3]$, $[Ru(fhma)_3]$ and $[Ru(bhma)_3]$ were successfully separated. When ethanol was used as developing solvent, most of the complexes showed almost the same R_f values (*ca.* 0.9) on both alumina and silica gel.

The separation of ruthenium(II) complexes was also tried by using ethanol and benzene–acetone (1 to 1 by volume). These results are presented in Table VI. On alumina, the ruthenium(II) complexes were oxidized to ruthenium(III) complexes. With the silica gel–(benzene–acetone) system, the separation of six ruthenium(II) complexes was successful, as was the separation of geometrical isomers of $K[Ru(bhfa)_3]$, $K[Ru(fhma)_3]$, and $K[Ru(fhpa)_3]$. A considerable difference of R_f value between $K[Ru(fhoa)_3]$ and $K[Ru(fhsa)_3]$ was observed.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 547045 from the Ministry of Education, Science and Culture. The authors thank Mrs Nakako TOKITA for her experimental assistance of elemental analyses, and Mrs Hiroko KIN for her experimental assistance of ^1H NMR spectrometry. Thanks are also due to Dr Scott Howell, Sophia University, for correcting the manuscript.

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