CHEMISTRY LETTERS, pp. 845-848, 1987.

Synthesis, Isolation, and Characterization of New Mixed-Ligand Ruthenium(III) Complexes with Two Kinds of β-Diketones

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A complete series of ruthenium(III) complexes with two kinds of ligands, acetylacetone and 1,1,1-trifluoro-4-phenyl-2,4-butanedione, was synthesized and isolated chromatographically. The isomers were characterized by means of NMR spectroscopy and X-ray single-crystal analysis. An inductive effect of ligand substituents on the methyne NMR signals is briefly discussed.

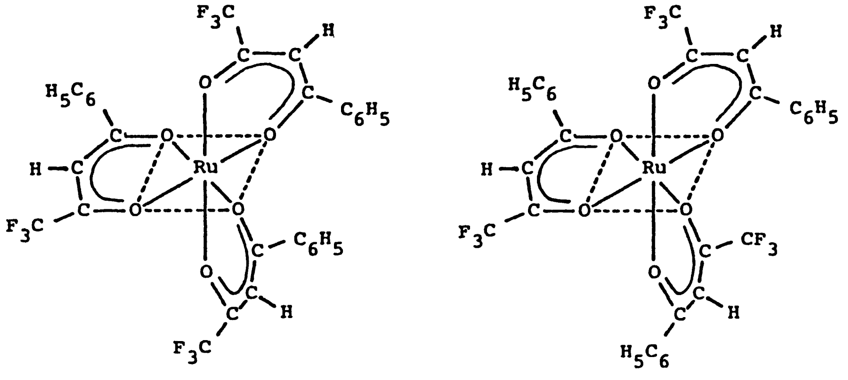
Octahedral complexes with two different β-diketones, in spite of their interesting properties, have not been investigated in detail owing to the difficulties in the synthesis, separation, and identification. So far, only one complete series of such mixed-ligand cobalt(III) complexes has been reported, whose members are separated and almost fully identified by means of NMR spectroscopy.1) Formation of some mixed-lignd β-diketonatoruthenium(III) complexes was described, but they were studied only in a mixture.2)

This paper deals with the synthesis, separation, and full identification of the complete series of compounds $[\mathrm{Ru}^{\mathrm{III}}(\mathrm{acac})_n(\mathrm{tfpb})_{3-n}]$ (n = 0,1,2 or 3), where acac^- is the anion of acetylacetone and tfpb^- is the anion of 1,1,1-trifluoro-4-phenyl-2,4-butanedione. The series comprises four members with different ligand compositions: $[\mathrm{Ru(tfpb)_3}]$ (**1**), $[\mathrm{Ru(acac)(tfpb)_2}]$ (**2**), $[\mathrm{Ru(acac)_2(tfpb)}]$ (**3**), $[\mathrm{Ru(acac)_3}]$ (**4**). Among them, **1** has two geometrical isomers and **2** has three (Fig. 1). Each of these complexes has a pair of optical isomers, but no attempt at resolving the optical isomers was made.

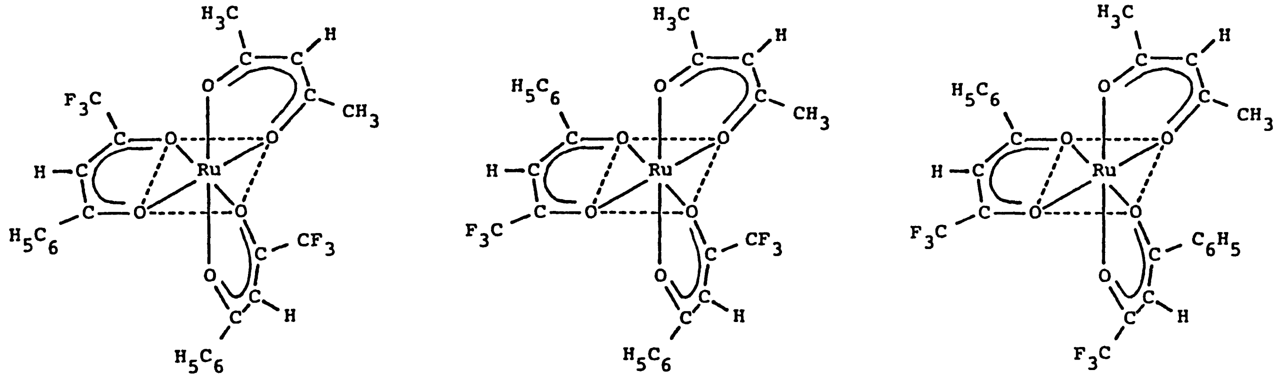
A crude mixture of the crystals of these complexes was readily obtained by using the "ruthenium blue" method.3) The two kinds of ligands were added to the "ruthenium blue solution" at one time. The total amount-of-substance ratio of the ligands to Ru was 3.3. The procedure of the isolation is summarized in Fig. 2.

Products F and G were identified as **3** and **4**, respectively, simply from the elemental analyses (Table 1). Characterization of products A, B, and D was achieved by ^{1}H NMR spectroscopy.4) Product A showed three signals from the methyne protons of tfpb^- ligand, whereas product B showed only one signal. Accordingly, product A is **1a**, which posseses C_1 symmetry, and product B is **1b**, which has C_3 symmetry. Product D gave rise to eleven signals, and products C and E six each (Fig. 3). Therefore, product D is identified as **2b**, which has no symmetry. Decisive discrimination between **2a** and **2c** is not possible from the NMR spectra, since both have C_2 symmetry.

A single-crystal of product C obtained from an aqueous ethanolic solution was subjected to X-ray analysis. As shown by a perspective drawing (Fig. 4), product C



1a *mer*-[Ru(tfpb)$_3$] **1b** *fac*-[Ru(tfpb)$_3$]



2a *trans*(CF$_3$)-*cis*(C$_6$H$_5$)-[Ru(acac)(tfpb)$_2$] **2b** *cis*(CF$_3$)-*cis*(C$_6$H$_5$)-[Ru(acac)(tfpb)$_2$] **2c** *cis*(CF$_3$)-*trans*(C$_6$H$_5$)-[Ru(acac)(tfpb)$_2$]

Fig. 1. Configuration of geometrical isomers of **1** and **2**.

Table 1. Elemental Analyses

Complex	Product	Formula	Ru(%)		C(%)		H(%)	
			Calcd	Found	Calcd	Found	Calcd	Found
1a	A	[Ru(tfpb)$_3$]	13.5	13.1	48.3	48.5	2.4	2.6
1b	B		13.5	a)	48.3	48.5	2.4	2.6
2a$^{b)}$	C	[Ru(acac)(tfpb)$_2$]	16.0	16.0	47.6	47.2	3.0	2.6
2b$^{b)}$	D		16.0	a)	47.6	47.7	3.0	3.0
2c$^{b)}$	E		16.0	a)	47.6	47.6	3.0	3.1
3$^{b)}$	F	[Ru(acac)$_2$(tfpb)]	19.6	19.9	46.7	46.7	3.9	4.2
4	G	[Ru(acac)$_3$]	25.4	26.9	45.2	44.9	5.3	5.1

a) Too small amounts of products B, D, and E were obtained to subject them to elemental analysis for ruthenium. b) New compounds.

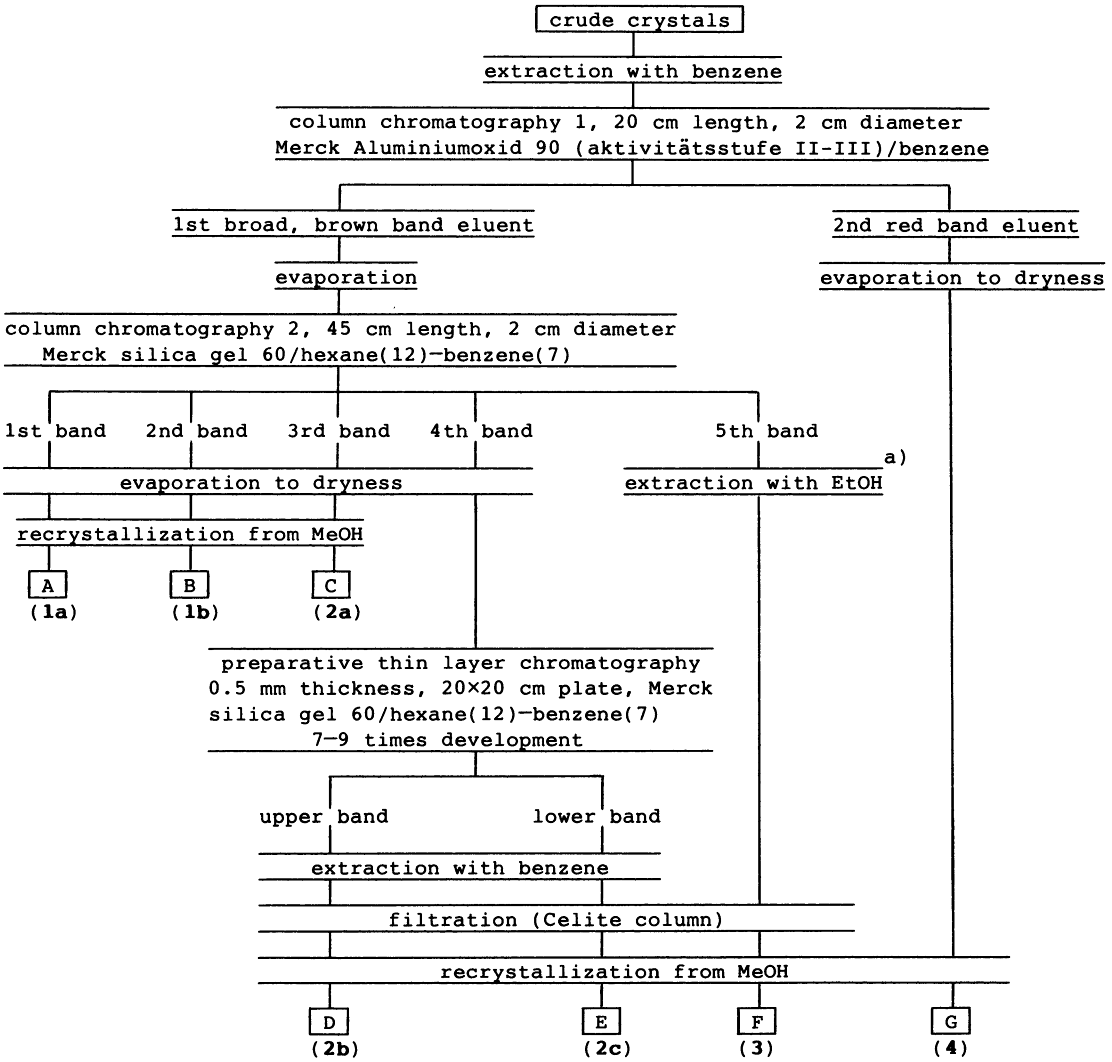


Fig. 2. Scheme of the isolation.

a) The red–brown band (5th band) was taken out of the column and extracted with ethanol.

is isomer **2a**. Then product E must be **2c**.

The chemical shifts of the methyne protons of **2a** and **2c** reflect an inductive effect of ligand substituents upon the environment of a methyne proton across the central metal. The positions *trans* to the oxygen atoms of acac$^-$ in **2c** are occupied by the trifluoromethyl ends of the tfpb$^-$ ligands, and these positions in **2a** by the phenyl ends of tfpb$^-$. Since trifluoromethyl is much more electron-withdrawing than phenyl, the unpaired-electron density on the acac$^-$ ring is reduced to a larger extent in **2c** than in **2a**; hence the CH (acac$^-$) signal of **2c** is at a lower field than that of **2a**. A similar effect is observed for the CH (tfpb$^-$) signals. This type of substituent effect may be generalized and made use of for identifying geometrical isomers of the same symmetry by means of NMR spectra.

The authors thank Professor Akira Ouchi of the University of Tokyo, and Associate Professor Mamoru Shimoi of Tohoku University, for the X-ray diffraction measurements and for their helpful discussions.

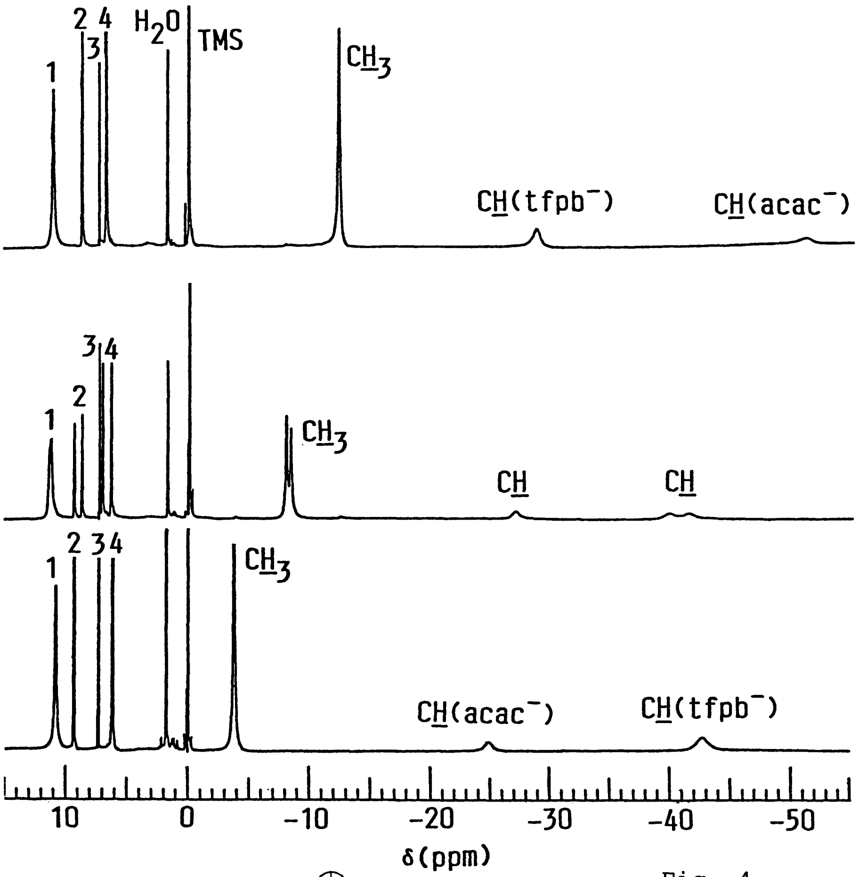


Fig. 3. ^1H NMR spectra in $CDCl_3$. C (**2a**), upper; D (**2b**), middle; E (**2c**), lower. 1, *o*-H; 2, *p*-H; 3, $CHCl_3$; 4, *m*-H. The assignment of the methyne protons in **2a** and **2c** are based on the ratio of the integral values.

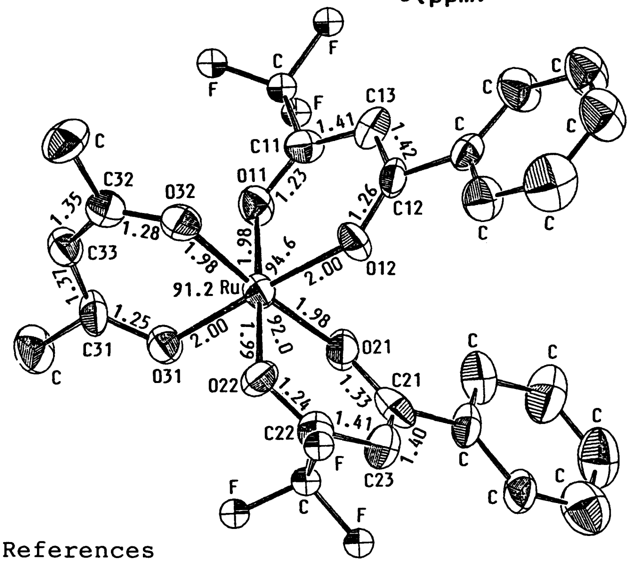


Fig. 4. Perspective drawing of product C (**2a**)[a] with some main bond lengths in 10^{-10} m and bond angles in degree.

[a] The crystals are orthorhombic, with the space group *Pbca*, a = 1.7970(6) nm, b = 1.8296(3) nm, c = 1.5762(3) nm, V = 5.182(2) nm^3, (Mo $K\alpha$) = 6.58 cm^{-1}, F.W. = 630.5, Z = 8, D_m = 1.59 g cm^{-3}, D_x = 1.62 g cm^{-3}. The structure was solved by the heavy atom method, and refined to give an R value of 0.108 for the 2389 independent reflections with $|F_o|>3\sigma(|F_o|)$. The reflections were collected by the θ-2θ scan technique ($2\theta<55°$) on a Rigaku AFC-6A automated four-circle diffractometer using Mo $K\alpha$ radiation (λ = 71.07 pm).

References

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4) ^1H NMR ($CDCl_3$) data for **1a** (A): δ = -49.7 (1H, s), -41.5 (1H, s), -21.7 (1H, s), 6.0 (2H, d, J = 6 Hz), 6.3 (2H, d, J = 6 Hz), 7.2 (2H, d, J = 6 Hz), 8.4 (1H, t, J = 6 Hz), 9.0 (1H, t, J = 6 HZ), 9.5 (1H, t, J = 6 Hz), 10.9 (4H), 11.5 (2H); for **1b** (B): δ = 35.5 (3H, s), 6.9 (6H, d, J = 6 Hz), 9.0 (3H, t, J = 6 Hz), 11.7 (6H).

(Received February 5, 1987)