CHEMISTRY LETTERS, pp. 437 - 440, 1984.

A NEW METHOD FOR SYNTHESIS OF RUTHENIUM(III) AND RUTHENIUM(II) COMPLEXES OF β-DIKETONES FROM "RUTHENIUM BLUE" SOLUTION

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The blue solution obtained by reducing hydrated ruthenium(III) trichloride with ethanol is used as a convenient starting material in the synthesis of several tris(β-diketonato)ruthenium(III) and tris(β-diketonato)ruthenate(II) complexes. The Hammett constants of the substituents on the ligand serve as a helpful guide for choosing the operating conditions.

"Ruthenium blue",[1)] the product 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.[2)] Shimizu[3)] reported that a blue material was readily obtained by reducing the ruthenium(III) salt with an ethanol-hydrochloric acid mixture and evaporating the reaction mixture to dryness. He prepared $[Ru(Hedta)(H_2O)]\cdot4H_2O$ 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[4,5)] for preparing some tris(β-diketonato)ruthenium(III) complexes. In fact, however, the addition of hydrochloric acid was unnecessary. In its absence, the reduction proceeds smoothly and the ligand can be added directly to the blue solution without evaporating it.

The present paper describes a new synthetic method for tris(β-diketonato)-ruthenium(III) and tris(β-diketonato)ruthenate(II) complexes, which are listed in Table 1. The seven ruthenium(III) complexes have been obtained in different, rather haphazard ways. In the method described below, on the contrary, only slight changes of the conditions are required for different β-diketones; furthermore, the necessary changes can be judged from the Hammett constants of the substituents on the ligand. This method is much faster than the previous methods and consumes smaller amounts of the β-diketones, which are quite expensive; reproducible results are also obtained with less skill.

Hydrated ruthenium trichloride (1 g, 4.4 mmol as Ru; Nakarai Chemicals Ltd.) was dissolved in a mixture of 50 cm^3 of water and 50–100 cm^3 ethanol. The 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 resulted in a poor yield and must be avoided. An excess amount of the ligand was introduced quickly, and the mixture was refluxed until its color turned red (about 30 min to 2–3 h, depending on the kind of the ligand). The mixture was cooled and a portion of potassium hydrogencarbonate was added, and the mixture was refluxed again for 1–2 h; this procedure was repeated. The color of the mixture gradually turned blue except in the cases of 6 and 7. After the addition of the last portion of the carbonate, refluxing was continued for 1–3 h. Up to this point, air should be excluded as far as possible. Then the solution was concentrated to *ca.* 50 cm^3 in a rotary evaporator. The precipitate which separated was collected by filtration and dried under a vacuum

The precipitate was extracted with *ca.* 20 cm^3 portions of benzene. The deep red benzene extract, which contained the ruthenium(III) species, was passed through a column of Merck Alminiumoxid 90 (aktivitätsstufe II–III), and the column was washed with benzene. The eluent was evaporated to dryness. The red residue was recrystallized from ethanol except for 4, which was recrystallized from benzene-ethanol (volume ratio, 1:1). When the ruthenium(II) species is stable in the air, as in the cases of 1', 2', and 3', it was obtained by extracting with acetone the residue of the benzene extraction and by concentrating the extract. The crystals were washed with benzene and dried under a vacuum.

In the above procedure, the amount-of-substance ratio of ligand to Ru was 3.3 for 1–6 and 4.5 for 7; the yield for 7 was a few percent when the ratio was 3.3. The amount-of-substance ratio of $KHCO_3$ to ligand was 1.5 for 1–5, 1.0 for 6 and 0.7 for 7. The carbonate should be added in several portions when the mixture is cooled. The carbonate was added in two equal portions for 1–6 and in three equal portions for **7**. In the case of **1**, the addition could be done at one time without any decrease in the yield.

Table 1. Yields of $[Ru^{III}L_3]$ and $K[Ru^{II}L_3]$ ($L=R'-CO-CH-CO-R''^{-}$) and sums of the Hammett constants of R' and R" ($\Sigma\sigma_m$)

No.[a)]	R'	R"	Yields/%	$\Sigma\sigma_m$[b)]
1	$-CF_3$	$-C_6H_5$	29.3	1.47
1'			55.4	
2	$-CF_3$	$-CH_3$	6.1	1.08
2'			57.6	
3	$-CF_3$	$-C(CH_3)_3$	11.9	0.99
3'			39.8	
4	$-C_6H_5$	$-C_6H_5$	46.5	0.36
5	$-C_6H_5$	$-CH_3$	77.6	-0.03
6	$-CH_3$	$-CH_3$	70.3	-0.41
7	$-C(CH_3)_3$	$-C(CH_3)_3$	30.3	-0.60

a) **1'**, **2'**, and **3'** are $K[Ru^{II}L_3]$; the others are $[Ru^{III}L_3]$.

b) Calculated from the values given by Murov.[7)]

Among the ten complexes in the Table, **1'**, **2'**, and **3'** are new compounds.[6)] They are readily soluble in acetonitrile, acetone, and ethanol giving blue solutions, but 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. When only the ruthenium(III) complexes are to be prepared, hydrogen peroxide may be added dropwise after the last refluxing until the color of the solution returns red.

In Table 1, the complexes are numbered in decreasing order (from positive to negative) of the reversible half-wave potential of the $[Ru^{III}L_3]/[Ru^{II}L_3]^-$ couple in acetonitrile.[5)] The more positive the half-wave potential is, the more relatively stable is the ruthenium(II) state with respect to the ruthenium(III) state. Indeed, **1'**, **2'**, and **3'** can be isolated and are fairly stable in air; in the cases of **4**, and **5**, the ruthenium(II) species were present in the reaction mixture, but they were oxidized when exposed to air during the subsequent handling. The half-wave potential is linearly related to the sum of the Hammett constants of the substituents on the ligands ($\Sigma\sigma_m$).[5)] It is inferred that a tris(β-diketonato)-ruthenate(II) complex can be obtained quite easily when $\Sigma\sigma_m$ is larger than *ca*. 1.0.

Interestingly, the order in Table 1 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. It seems that the smaller $\Sigma\sigma_m$ is, the less easy the complex formation becomes. In the synthesis of a complex having a negative $\Sigma\sigma_m$ value, the addition of a larger excess of the ligand and milder conditions for the neutralization will be preferable.

This observation can be explained as follows. If the metal-ligand σ-bonds are rather insensitive to the electron-accepting power of substituents R' and R", the relative stability of the complex will be decided mainly by the back donation. Electron-accepting substituents, with larger $\Sigma\sigma_m$ values, will lower the energy level of the ligand LUMOs and consequently will facilitate the back donation from the t_{2g} orbitals of the central atom.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 547045 from the Ministry of Education, Science and culture. Thanks are also due to Dr. F. Scott Howell, Sophia University, for correcting the manuscript.

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6) Elemental Analysis. For **1**', Found: C, 46.4; H, 2.1%. Calcd for $K[RuC_{30}H_{18}O_6F_9]$: C, 45.9; H, 2.3%. For **2**', Found: C, 30.0; H, 2.1; Ru, 16.5%. Calcd for $K[RuC_{15}H_{12}O_6F_9]$: C, 30.1; H, 2.0; Ru, 16.9%. For **3**', Found: C, 39.5; H, 4.2; Ru, 13.3%. Calcd for $K[RuC_{24}H_{30}O_6F_9]$: C, 39.7; H, 4.2; Ru. 13.9%.
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(Received December 17, 1983)