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PREPARATION OF TRIS(3-SUBSTITUTED ACETYLACETONATO)RUTHENIUM(III) COMPLEXES AND THEIR ELECTROCHEMICAL BEHAVIOR IN ACETONITRILE

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Four tris(3-substituted acetylacetonato)ruthenium(III) complexes were newly synthesized and their electrochemical oxidation and reduction were investigated in acetonitrile. The oxidation and reduction potentials of $[Ru^{III}(R'\text{-CO-CR-CO-}R'')_3]$ can be expressed as a linear function of the sum of the Hammett constants, if one uses the para-position value for R and the meta-position values for R' and R".

A number of tris(2,4-substituted acetylacetonato)ruthenium(III) complexes, $[Ru^{III}(R'\text{-CO-CH-CO-}R'')_3]$, have been prepared.[1)] They undergo one-electron oxidation to the ruthenium(IV) species as well as reduction to the ruthenium(II) species in aqueous[2)] or nonaqueous solutions.[3-5)] The reversible half-wave potentials ($E^{r}_{1/2}$) of these steps were found to be linearly dependent on the sum of the Hammett constant values for the meta-position of the substituents on the ligands.[3-5)] A similar substituent effect is expected for the tris(3-substituted acetylacetonato)ruthenium(III) complexes, $[Ru^{III}(CH_3\text{-CO-CR-CO-}CH_3)_3]$. Only two complexes of this type have been synthesized: tris(3-phenylacetylacetonato)-[3)] and tris(3-vinylferrocenylacetylacetonato)ruthenium(III).[6)] This report deals with the synthesis of four new complexes (R = Cl, Br, I, and CH_3) and their reduction-oxidation at a platinum electrode in acetonitrile (AN).

The halogenated complexes (**1**–**3**) were prepared by the direct substitution of the 3-position of the ligands of tris(acetylacetonato)ruthenium(III). *N*-Halogenosuccinimide (XNR; X = Cl, Br, I) was added to a chloroform solution (in the case of **1** and **2**) or a benzene solution (in the case of **3**) of **4**. The amount-of-substance ratio of XNR to 4 was 4.5 for 1, 3.0 for 2, and 9.0 for 3. BrNR immediatly reacted with 4 to give 2. However, 1 was obtained by letting the mixture stand overnight, and 3 was obtained by refluxing the mixture for *ca*. 1 h. It was noted that in the cases of 1 and 2, excessive addition of ClNR or BrNR resulted in the decomposition of both the starting complex and the product. The resulting solution was passed through a column of Merck Aluminumoxid 90 (Activitätsstufe II–III) (in the case of 1, it was necessary to evaporate off the solvent and to extract the residue with benzene). The eluent was evaporated to dryness. The residue was recrystallized from ethanol and the crystals were dried under a vacuum.[7)] Interestingly, when the benzene solution of iodine monochloride, which is known to be an iodination reagent in chloroform or acetate buffer,[8)] was introduced to the benzene solution of 4, not 3-iodo complex, but 3-chloro complex was produced with *ca*. 100% yield.

The other 3-substituted complexes (5 and 6) were prepared by an indirect method: the 3-substituted acetylacetones were prepared separately and then ligated to ruthenium by means of the "ruthenium blue solution" method.[1)] 3-Methylacetylacetone was synthesized by refluxing acetylacetone and methyliodide in the presence of potassium carbonate in acetone.[9)]

Each of the tris(3-substituted acetylacetonato)ruthenium(III) complexes in

Table 1. The reversible half-wave potentials ($E^{r}_{1/2}$) and the diffusion coefficients (D) of $[Ru^{III}(CH_3\text{-CO-CR-CO-}CH_3)_3]$ in 0.1 mol dm^{-3} $[(C_2H_5)_4N](ClO_4)$–acetonitrile solutions at 25 °C

Complex[a)]	R	Yield/%	$\Sigma\sigma_{m,p}$[b)]	$E^{r}_{1/2}/V$[c)] reduction	$E^{r}_{1/2}/V$[c)] oxidation	$D/10^{-10}$ m^2 s^{-1}
1	Cl	42[d)] , 100[e)]	+0.27	-0.82	+0.80	12.6
2	Br	100	+0.27	-0.81	+0.79	11.3
3	I	84	+0.12	-0.84	+0.73	12.4
4	H	70	-0.42	-1.14	+0.63	14.4
5	C_6H_5	33	-0.45	-1.21	+0.53	10.5
6	CH_3	21	-0.93	-1.30	+0.35	13.6

a) 1, 2, 3, and 6 are new compounds. b) $\Sigma\sigma_{m,p} = 3(2\sigma_m(CH_3) + \sigma_p(R))$ c) Against Ag|0.1 dm^{-3} AgClO$_4$, AN; obtained from the normal pulse voltammograms at platinum electrode. d) From *N*-chlorosuccinimide. e) From iodinemonochloride.

Table 1 showed an oxidation step and a reduction step, both with diffusion-controlled limiting currents in 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP)-AN solution at platinum disk electrodes. The cyclic voltammogram showed a pair of anodic and cathodic peaks of equal height corresponding to the oxidation and the reduction steps. In every case, the ln-plot analysis of the steps revealed that the oxidation and the reduction steps were Nernstian, one-electron processes to the corresponding Ru^{IV} and Ru^{II} species, respectively.

In Fig. 1, the reversible half-wave potentials (Table 1) were plotted against the sum of the Hammett constants of the substituents, $\Sigma\sigma_{m,p}$. Here the value of $\Sigma\sigma_{m,p}$ is calculated by using the para-position value of the Hammett constants for R and the meta-position value for the methyl groups; that is $\Sigma\sigma_{m,p} = 3(2\sigma_m(CH_3) + \sigma_p(R))$. The plots lie along straight lines which are almost identical with the lines drawn for the 2,4-substituted complexes.[5] If the meta-position values of the Hammett constants for the 3-substituents are used, the plot becomes more scattered and deviates from the lines for the 2,4-substituted complexes. This fact is understandable since the 3-position of the ligand can be regarded as the para position with respect to the ruthenium atom in the six-membered chelate ring. In conclusion, each the oxidation and reduction potentials of $[Ru^{III}(R'\text{-CO-CR-CO-}R'')_3]$ can be expressed as a linear function of the sum of the Hammett constants, if one uses the para-position value for R and the meta-position values for R' and R"; $\Sigma\sigma_{m,p} = 3(\sigma_m(R') + \sigma_p(R) + \sigma_m(R''))$.[10]

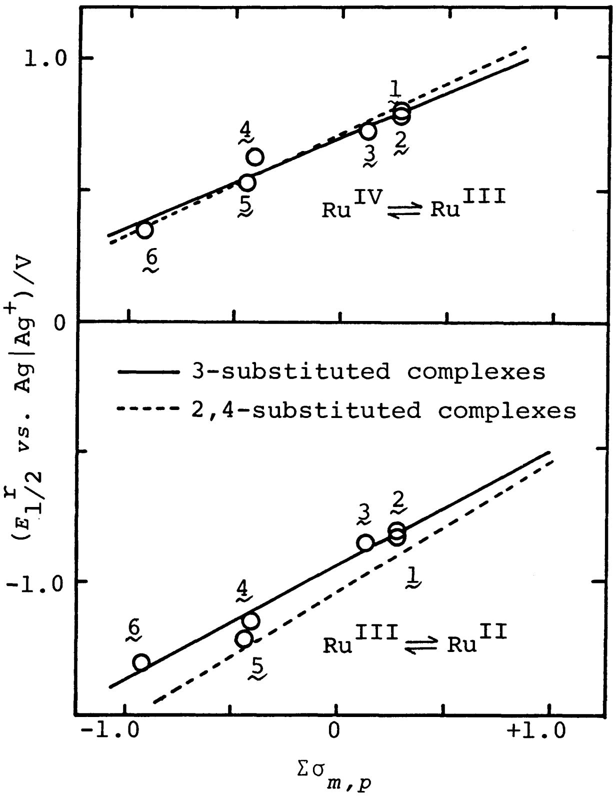

Fig. 1. The relationships between $E^r_{1/2}$ and the sum of the Hammett constant.

The values of the diffusion coefficients of the 3-substituted complexes obtained by means of the Levich equation are also presented in Table 1. The diffusion coefficient changes appreciably with the bulkiness of the substituent. The value of the 3-phenyl substituted complex is the same as that of tris(1-phenyl-1,3-propanedionato)ruthenium(III) (10.7×10^{-10} m^2 s^{-1}).5) This suggests that the diffusion coefficients of the β-diketonato complex is decided mainly by the bulkiness of the substituent, while its position has little effect.

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7) Elemental analysis. For **1**, Found: C, 37.1; H, 3.6; Ru, 20.1%. Calcd for [$RuC_{15}H_{18}O_6Cl_3$]: C, 35.9; H, 3.6; Ru, 20.1%. For **2**, Found: C, 27.3; H, 2.7; Ru, 14.9%. Calcd for [$RuC_{15}H_{18}O_6Br_3$]: C, 28.4; H, 2.9; Ru, 15.9%. For **3**, Found: C, 23.5; H, 2.3; Ru, 12.0%. Calcd for [$RuC_{15}H_{18}O_6I_3$]: C, 23.3; H, 2.3; Ru, 13.0%. For **6**, Found: C, 48.7; H, 6.1; Ru, 23.6%. Calcd for [$RuC_{18}H_{27}O_6$]: C, 49.1; H, 6.2; Ru, 22.9%.

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10) R', R" = $-CH_3$, $-CF_3$, $-C_6H_5$, $-C(CH_3)_3$,  ,  .5)

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