Bull. Chem. Soc. Jpn., 70, 1069—1075 (1997)

Facile Chemical Dehydrogenation of α-Amino Acids Chelated to a Ruthenium(II) Ion: (α-Imino acidato)bis(1,10-phenanthroline)ruthenium(II) Complexes[1)]

Tomonori Mori, Tadayoshi Yamamoto, Motowo Yamaguchi,* and Takamichi Yamagishi

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-03

(Received November 20, 1996)

(α-Amino acidato)ruthenium(II) complexes were dehydrogenated to give (α-imino acidato)ruthenium(II) complexes by chemical oxidation. (α-Imino acidato)ruthenium(II) complexes, $[Ru^{II}\{N(R^1)=C(R^2)CO_2\}(phen)_2]^+$ (R^1 = H, Me, or Bn, R^2 = H; R^1 = H or Me, R^2 = Me; R^1, R^2 = $-(CH_2)_3-$) were obtained from the (α-amino acidato)ruthenium(II) complexes (glycinato, *N*-Me-glycinato, *N*-Bn-glycinato, (*S*)-alaninato, *N*-Me-(*S*)-alaninato, and (*S*)-prolinato complexes) by using diammonium cerium(IV) nitrate (CAN) as an oxidizing reagent. On the other hand, in the presence of hydrogen peroxide, the α-imino acidato complexes were converted to the corresponding α-imino acidato complexes, except for the glycinato and (*S*)-alaninato complexes. In particular, the iminoacetatoruthenium(II) complex, $[Ru(NH{=}CHCO_2)(phen)_2]^+$, was synthesized for the first time by this method using CAN as an oxidizing reagent. Dehydrogenation with CAN is more facile and versatile than any other method that we have ever examined.

α-Amino acids are partially metabolized through oxidative deamination to α-keto acids by enzymes, such as amino acid oxidase or dehydrogenase. At the first step of this reaction, α-amino acids are dehydrogenated to yield α-imino acids. α-Imino acids are unstable in an aqueous solution, and are easily hydrolyzed to afford α-keto acids. On the contrary, chelation to a metal ion stabilizes α-imino acids, and α-imino acidato complexes are isolated. α-Imino acidato complexes of the Co(III),[2—7)] Ru(II),[8)] Pd(II),[9)] and Mo(II)[10)] ions have been reported, which were prepared by several methods. (α-Imino acidato)ruthenium(II) complexes could be potential synthetic building blocks for various α-amino acidato complexes, since the reactive C=N bond would be attacked by nucleophilic reagents.[2,11,17)]

We have already reported on a novel dehydrogenation of the (α-amino acidato)cobalt(III) complexes by chemical oxidation[3)] and Ru(II) complexes by electrolysis at a constant potential.[8)] However, there are several disadvantages in electrolysis at a constant potential: The reaction time is rather long, and a special instrument is necessary. Furthermore, attempted electrolysis at a constant potential of the glycinatoruthenium(II) complex $[Ru(gly)(phen)_2]^+$ has failed to afford the corresponding α-imino acidato complex,[12)] which would be the simplest α-imino acidato complex. The amine, diamine, or polyamine ruthenium(II) complexes have been dehydrogenated to the imine, diimine, or polyimine ruthenium(II) complexes by either chemical or anodic oxidation.[13—15)] Hence, the chemical oxidation of α-amino acidato complexes using effective oxidizing reagents was examined, which would be more facile and versatile than electrolysis at a constant potential.

For example, the cerium(IV) ion is widely applicable in the oxidation of various organic compounds[16)] and transition metal complexes. The Ru(II) complexes of 1,2-diamines are easily dehydrogenated to the 1,2-diimine complexes by using the Ce(IV) ion.[14)] Hydrogen peroxide might also be an effective oxidizing reagent for the dehydrogenation of (α-amino acidato)ruthenium(II) complexes.

We now report on the dehydrogenation of (α-amino acidato)bis(1,10-phenanthroline)ruthenium(II) complexes, $[Ru^{II}\{NH(R^1)-CH(R^2)CO_2\}(phen)_2]^+$ (R^1 = H, Me, or Bn, R^2 = H; R^1 = H, or Me, R^2 = Me; R^1, R^2 = $-(CH_2)_3-$; phen = 1,10-phenanthroline), by chemical oxidation using ammonium cerium(IV) nitrate (CAN) and hydrogen peroxide as the oxidizing reagent to yield the corresponding (α-imino acidato)ruthenium(II) complexes, $[Ru^{II}\{N(R^1){=}C(R^2)CO_2\}(phen)_2]^+$. By using CAN as the oxidizing reagent, the iminoacetatoruthenium(II) complex, the simplest α-imino acidato complex with no substituent group on the C=N group, which cannot be obtained by electrolysis at a constant potential, was successfully synthesized for the first time.[17)]

Experimental

Materials. All of the chemicals were of reagent grade, and were used as received. *cis*-Dichlorobis(1,10-phenanthroline)ruthenium(II) was prepared by a method similar to that of the bis(2,2′-bipyridine) complex.[18)]

Instrumentation and Measurements. The electronic absorption spectra were measured with a Hitachi 220A spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer. The chemical shifts were reported on the δ scale in ppm relative to tetramethylsilane (TMS) or sodium 4,4-dimethyl-4-silapentanoate-d_4 (TSP) for ^{1}H NMR and to 1,4-dioxane (67.4

ppm) for ^{13}C NMR. The fast atom bombardment (FAB) mass spectra were measured with a JEOL JMS-DX300 spectrometer using *m*-nitrobenzyl alcohol as a matrix. All of the electrochemical measurements were made versus the saturated calomel electrode (SCE), and were uncorrected for junction potentials. The potential control for electrochemical experiments was obtained with a Hokuto Denko Model HA-501 potentiostat/galvanostat. The waveform generator was a Hokuto Denko Model HB-104 function generator. Cyclic voltammetric experiments were conducted in a two-compartment electrochemical cell equipped with a platinum working electrode, a platinum counter electrode, and a saturated calomel reference electrode, which was separated by a salt bridge. All of the solutions were deoxygenated by bubbling nitrogen gas through them and were maintained under nitrogen during the experiments.

General Procedure for Preparing (α-Amino acidato)-ruthenium(II) Complexes: [Ru(α-amino acidato)(phen)$_2$]X (X=Cl, ClO$_4$ or PF$_6$). The (α-amino acidato)bis(1,10-phenanthroline)ruthenium(II) complexes were prepared by a method described in the literature.[8,19] To a hot solution of [RuCl$_2$(phen)$_2$] in 50% aqueous ethanol was added an aqueous solution of amino acid and NaOH; the mixture was refluxed for 1 h. The pH was adjusted to 7 with 1.0 mol dm^{-3} HCl. The reaction mixture was concentrated and desalted, then poured onto a column of SP-Sephadex C-25 cation-exchange resin in the sodium form. The complex was eluted with 0.1 mol dm^{-3} NaCl. The concentration of the eluate from the main band gave a reddish-orange powder, which was recrystallized from ethanol and ethyl acetate.

[Ru(gly)(phen)$_2$]Cl·2H$_2$O 1. Yield: 67%. ^1H NMR (D$_2$O, 270 MHz), δ_H = 3.60 (dd, 1H, C*H*, *J* = 6.3, 17 Hz), 3.87 (dt, 1H, C*H*, *J* = 7.1, 17 Hz), 4.15 (m, 1H, N*H*), 4.9 (1H, N*H*), 7.2—9.7 (m, 16H, aromatics). Selected data of ^{13}C NMR (D$_2$O, 67.5 MHz), δ_C = 46.5 (*C*H$_2$), 125—155 (aromatics), 186.5 (*C*=O). Anal. Found: C, 51.25; H, 3.52; N, 11.68%. Calcd for C$_{26}$H$_{24}$N$_5$O$_4$ClRu: C, 51.45; H, 3.99; N. 11.54%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 482 (1.19×10^4), 450(sh) (1.06×10^4), 316(sh) (3.54×10^3), 265 (6.75×10^4), and 223 (5.13×10^4). FAB mass: *m/z* 536 (M−Cl)$^+$.

[Ru(*N*-Me-gly)(phen)$_2$]Cl·3.5H$_2$O 2. Yield: 80%. ^1H NMR (D$_2$O, 270 MHz), δ_H = 1.60 (d, N–C*H*$_3$(II), *J* = 5.9 Hz), 2.37 (d, N–C*H*$_3$(I), *J* = 5.9 Hz), 3.39 (dd, C*H*(II), *J* = 7.4, 17 Hz), 3.85 (dd, C*H*(I), *J* = 4.9, 12 Hz), 4.0 (m, C*H*(I)), 4.04 (dd, C*H*(II), *J* = 6.6, 17 Hz), 5.08 (m, N*H*(I)), 5.61 (m, N*H*(II)), 7.2—9.9 (m, 16H, aromatics). ^{13}C NMR (D$_2$O, 67.5 MHz), δ_C = 39.7 (N–*C*H$_3$(II)), 39.8 (N–*C*H$_3$(I)), 57.6 (*C*H$_2$(II)), 57.8 (*C*H$_2$(I)),125—155 (aromatics), 184.1 (*C*=O(II)), 184.7 (*C*=O(I)). Anal. Found: C, 49.60; H, 4.24; N, 11.12%. Calcd for C$_{27}$H$_{29}$N$_5$O$_{5.5}$ClRu: C, 50.04; H, 4.51; N, 10.81%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 479 (1.00×10^4), 459(sh) (9.85×10^3), 315(sh) (4.99×10^3), 265 (6.33×10^4), and 223 (5.00×10^4). FAB mass: *m/z* 550 (M−Cl)$^+$.

[Ru(*N*-Bn-gly)(phen)$_2$]Cl·2H$_2$O 3. Yield: 34%. ^1H NMR (D$_2$O, 270 MHz), δ_H = 3.24 (dd, C*H*(gly)(II), *J* =10, 14 Hz), 3.68 (dd, C*H*(gly)(I), *J* = 5.6, 17 Hz), 3.76 (dd, C*H*(gly)(II), *J* = 4.0, 14 Hz), 4.03 (dd, C*H*(Bn)(I), *J* = 5.1, 17 Hz), 4.1—4.4 (m, C*H*(gly)(I), C*H*$_2$(Bn)(I), C*H*(Bn)(II)), 5.02 (m, N*H*(I)), 5.96 (m, N*H*(II)), 6.2—10.1 (m, aromatics). ^{13}C NMR (D$_2$O, 67.5 MHz), δ_C = 57.5 (*C*H$_2$(gly)(I)), 58.6 (*C*H$_2$(Bn)(I)), 58.8 (*C*H$_2$(Bn)(II)), 59.6 (*C*H$_2$(gly)(II)),125—156 (aromatics), 182.7 (*C*=O), 183.4 (*C*=O). Anal. Found: C, 56.83; H, 4.42; N, 10.16%. Calcd for C$_{33}$H$_{30}$N$_5$O$_4$ClRu: C, 56.85; H, 4.34; N. 10.05%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 477 (1.03×10^4), 430(sh) (8.86×10^3), 317(sh) (3.39×10^3), 265 (6.22×10^4), and 222 (4.89×10^4). FAB mass: *m/z* 626 (M−Cl)$^+$.

[Ru((*S*)-ala)(phen)$_2$]PF$_6$·2.5H$_2$O 4. Yield: 50%. ^1H NMR (D$_2$O, 270 MHz), δ_H = 1.46 (d, C–C*H*$_3$(II), *J* = 6.9 Hz), 1.62 (d, C–C*H*$_3$(I), *J* = 7.3 Hz), 3.63 (m, C*H*(I)), 3.82 (m, N*H*(II)), 4.07 (m, C*H*(II)), 4.43 (m, N*H*(I)), 4.64 (m, N*H*(I)), 5.47 (m, N*H*(II)), 7.2—9.8 (m, 16H, aromatics). ^{13}C NMR (D$_2$O, 67.5 MHz), δ_C = 20.6, 20.7 (*C*H$_3$), 52.8, 53.5 (*C*H), 125—156 (aromatics), 187.7, 188.1 (*C*=O). Anal. Found: C, 43.54; H, 3.27; N, 9.78%. Calcd for C$_{27}$H$_{27}$N$_5$O$_{4.5}$PF$_6$Ru: C, 43.85; H, 3.68; N. 9.47%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 483 (1.03×10^4), 460(sh) (1.00×10^4), 316(sh) (4.59×10^3), 265 (6.52×10^4), and 223 (5.16×10^4). FAB mass: *m/z* 550 (M−PF$_6$)$^+$.

[Ru(*N*-Me-(*S*)-ala)(phen)$_2$]Cl·4H$_2$O[8] 5. Yield: 77%.

[Ru((*S*)-pro)(phen)$_2$]Cl·3.5H$_2$O[8] 6. Yield: 73%.

Measurements of the Electronic Absorption or Nuclear Magnetic Resonance Spectra of (α-Amino acidato)ruthenium(II) Complexes in the Presence of Hydrogen Peroxide. To an aqueous solution of [Ru(α-amino acidato)(phen)$_2$]X was added an equivalent amount of hydrogen peroxide. The spectra (electronic absorption, NMR or FAB MS) were measured periodically at an appropriate interval.

Measurement of the Electronic Absorption Spectra of (α-Amino acidato)ruthenium(II) Complexes with the Addition of CAN. Under nitrogen, to an aqueous solution of [Ru(α-amino acidato)(phen)$_2$]X was added an aqueous CAN solution by 0.25 equivalence to the complex until two equivalents. After each addition of an aqueous solution of CAN, the electronic absorption spectrum was measured.

General Procedure for Preparing (α-Imino acidato)-ruthenium(II) Complexes, [Ru(α-imino acidato)(phen)$_2$]X (X=Cl, ClO$_4$ or PF$_6$), Using CAN. To an aqueous solution (20 cm^3) of [Ru(α-amino acidato)(phen)$_2$]X (0.08 mmol) was added an aqueous solution (10 cm^3) of two equivalents of CAN (0.16 mmol) under nitrogen with stirring. The reaction mixture was quickly poured onto a column of SP-Sephadex C-25 cation-exchange resin in the sodium form. The complex was eluted with 0.1 mol dm^{-3} NaCl. The concentration of the eluate from the main band gave a reddish-orange powder, which was recrystallized from ethanol and ethyl acetate.

[Ru(gly-H$_2$)(phen)$_2$]ClO$_4$·1.5H$_2$O 7. Yield: 58%. ^1H NMR (D$_2$O, 270 MHz), δ_H = 7.3—9.2 (m, 17H, C*H* and aromatics). ^{13}C NMR (D$_2$O, 67.5 MHz), δ_C = 127—157 (aromatics), 171.1 (*C*=N), 178.6 (*C*=O). Anal. Found: C, 47.34; H, 2.97; N, 10.84%. Calcd for C$_{26}$H$_{21}$N$_5$O$_{7.5}$ClRu: C, 47.32; H, 3.21; N. 10.61%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 444 (9.77×10^3), 314(sh) (4.40×10^3), 263 (6.62×10^4), and 221 (5.79×10^4). FAB mass: *m/z* 534 (M−ClO$_4$)$^+$.

[Ru(*N*-Me-gly-H$_2$)(phen)$_2$]ClO$_4$·1.5H$_2$O 8. Yield: 77%. ^1H NMR (CD$_3$OD, 270 MHz), δ_H=3.20 (d, 3H, N–C*H*$_3$, *J*=1.7 Hz), 8.1 (q, 1H, C*H*, *J*=1.7 Hz), 7.4—9.2 (m, 16H, aromatics). ^{13}C NMR (CD$_3$OD, 67.5 MHz), δ_C = 49.2 (N–*C*H$_3$), 126—155 (aromatics), 166.8 (*C*=N), 175.5 (*C*=O). Anal. Found: C, 47.99; H, 3.27; N, 10.35%. Calcd for C$_{27}$H$_{23}$N$_5$O$_{7.5}$ClRu: C, 48.11; H, 3.44; N. 10.39%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 450 (1.32×10^4), 425(sh) (1.26×10^4), 314(sh) (4.63×10^3), 263 (7.55×10^4), and 222 (6.01×10^4). FAB mass: *m/z* 548 (M−ClO$_4$)$^+$.

[Ru(*N*-Bn-gly-H$_2$)(phen)$_2$]ClO$_4$·1.5H$_2$O 9. Yield: 87%. ^1H NMR (CD$_3$OD, 270 MHz), δ_H = 5.08 (dd, 1H, Ph–C*H*, *J* = 1.4, 13 Hz), 5.41 (d, 1H, Ph–C*H*, *J* = 13 Hz), 5.9—6.6 (m, 5H, Ph), 8.48 (d, 1H, C*H*=N, *J* = 1.4 Hz), 7.2—9.4 (m, 16H, aromatics). ^{13}C NMR (CD$_3$OD, 67.5 MHz), δ_C = 68.5 (*C*H$_2$), 125—155 (aromatics), 167.7 (*C*=N), 175.7 (*C*=O). Anal. Found: C, 52.62; H, 3.63; N, 9.55%. Calcd for C$_{33}$H$_{27}$N$_5$O$_{7.5}$ClRu: C, 52.84; H, 3.63; N.

9.34%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 456 (1.40×10^4), 430(sh) (1.31×10^4), 315(sh) (3.92×10^3), 264 (6.68×10^4), and 222 (5.30×10^4). FAB mass: *m/z* 624 $(M-ClO_4)^+$.

[Ru(ala-H$_2$)(phen)$_2$]PF$_6$·2.5H$_2$O 10. Yield: 73%. ^{1}H NMR (D_2O, 270 MHz), δ_H = 2.37 (s, 3H, C–C*H*$_3$), 7.2—9.1 (m, 16H, aromatics). ^{13}C NMR (D_2O, 67.5 MHz), δ_C = 22.9 (C–*C*H$_3$), 125—155 (aromatics), 176.0, 176.6 (*C*=N, *C*=O). Anal. Found: C, 43.97; H, 3.42; N, 9.50%. Calcd for $C_{27}H_{25}N_5O_{4.5}PF_6Ru$: C, 44.21; H, 3.30; N. 8.84%. Electronic absorption data, λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 460(sh) (1.21×10^4), 440 (1.24×10^4), 314(sh) (3.83×10^3), 263 (6.67×10^4), and 222 (4.94×10^4). FAB mass: *m/z* 548 $(M-PF_6)^+$.

[Ru(*N*-Me-ala-H$_2$)(phen)$_2$]ClO$_4$[8] 11. Yield: 66%.

[Ru(pro-H$_2$)(phen)$_2$]ClO$_4$·0.5H$_2$O[8] 12. Yield: 57%.

Results and Discussion

Syntheses of (α-Amino acidato)ruthenium(II) Complexes. The treatment of *cis*-[RuCl$_2$(phen)$_2$] with sodium α-amino acidate in hot ethanol–water (1 : 1) affords the (α-amino acidato)bis(1,10-phenanthroline)ruthenium(II) complexes ([Ru(α-amino acidato)(phen)$_2$]X : α-amino acidato = glycinato, *N*-methylglycinato, *N*-benzylglycinato, (*S*)-alaninato, *N*-methyl-(*S*)-alaninato or (*S*)-prolinato; X = Cl, ClO_4 or PF_6). The NMR spectra of these complexes reveal that they consist of approximately equal amounts of two diastereomers, except that of the glycinato complex: *Δ*-*S* and *Λ*-*S* for the (*S*)-alaninato or (*S*)-prolinato complexes and *Δ*-*S*/*Λ*-*R* and *Λ*-*S*/*Δ*-*R* for the *N*-methylglycinato, *N*-benzylglycinato or *N*-methyl-(*S*)-alaninato complexes. For the *N*-methylglycinato, *N*-benzylglycinato or *N*-methyl-(*S*)-alaninato complexes, the NMR peaks of two isomers shown in experimental section (isomers I and II) were assigned based on the HH COSY spectra. Isomer II was assumed to be *Λ*-*S*/*Δ*-*R*, because its *N*-methyl group resonates at a higher magnetic field compared to that of isomer I, due to the ring current effect of 1,10-phenanthroline.

Dehydrogenation of (α-Amino acidato)ruthenium(II) Complexes by Chemical Oxidation. (α-Imino acidato)-ruthenium(II) complexes, such as 2-methyliminopropionato or 1-pyrroline-2-carboxylatoruthenium(II) complexes, have been prepared from the corresponding α-amino acidato complexes by anodic oxidation.[3] However, anodic oxidation of the glycinato complex failed to give the α-imino acidato complex. We therefore examined the chemical oxidation of the glycinato complex.

First, we employed hydrogen peroxide as an oxidizing reagent. In the presence of hydrogen peroxide, the α-amino acidato complexes are slowly converted to the α-imino acidato complexes, except for the glycinato and (*S*)-alaninato complexes. After 72 h, particular peaks of the α-amino acidato complexes disappeared, and those of the α-imino acidato complexes were observed by NMR and FAB MS spectra. As for the UV/visible spectra, the absorption maximum in the visible region shows a blue shift, indicating the formation of the α-imino acidato complexes.[8] However, since those spectra do not have an isosbestic point, the reaction using hydrogen peroxide as an oxidant is not quantitative, and produces by-products. It is assumed that a part of the α-imino acidato complex may be further oxidized. In the case of the glycinato or (*S*)-alaninato complexes, which contain the NH_2-group with no substituent, no α-imino acidato complex, such as iminoacetato ($NH{=}CHCO_2^-$) or 2-iminopropionato ($NH{=}C(Me)CO_2^-$), was obtained, probably due to successive oxidation. Using hydrogen peroxide as an oxidizing reagent, *N*-alkyl substituted α-amino acidato complexes were partly dehydrogenated to give the corresponding α-imino acidato complexes; though these reactions were not quantitative.

On the other hand, it was found that ammonium cerium(IV) nitrate (CAN) is more facile and versatile than electrolysis at a constant potential and other oxidizing reagents to dehydrogenate α-amino acidato complexes giving α-imino acidato complexes. Figure 1 shows the change in the electronic absorption spectrum of the glycinato complex ([Ru(gly)(phen)$_2$]$^+$) of CAN by a 0.25 equivalent portion. The dehydrogenation by CAN is so fast that the spectrum is changed immediately with the addition of CAN. The spectrum of the α-amino acidato complex changes with an isosbestic point at 473 nm, and those of the other (α-amino acidato)ruthenium(II) complexes show a similar behavior upon the addition of CAN. The spectra show an isosbestic point until the addition of two equivalents of CAN. Then, the α-amino acidato complexes were oxidized on a preparative scale by two equivalents of CAN to afford the products, which were assigned by measurements of the FAB-MS and NMR spectra to be the α-imino acidato complexes. The dehydrogenation of the α-amino acidato complexes, giving rise to the α-imino acidato complexes, is a two-electron oxidation process (Scheme 1). Consequently, α-imino acidato complexes were quantitatively obtained with the addition of two equivalents of CAN. There are four possible types of the (α-imino acidato)ruthenium(II) complexes: with or without

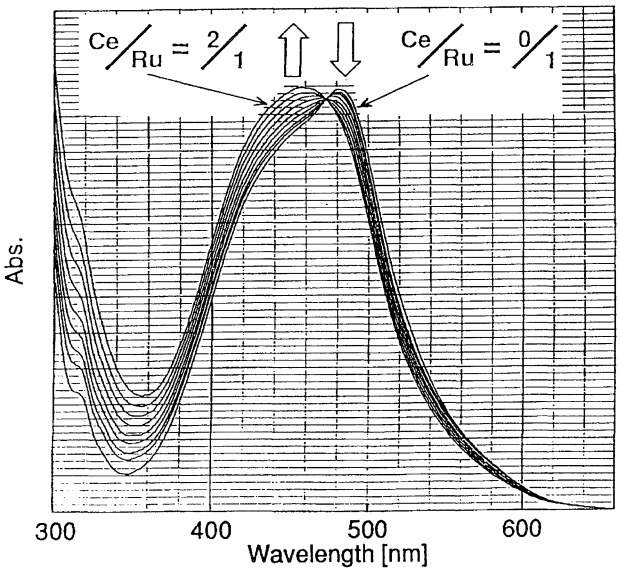
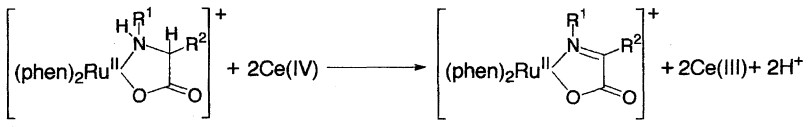
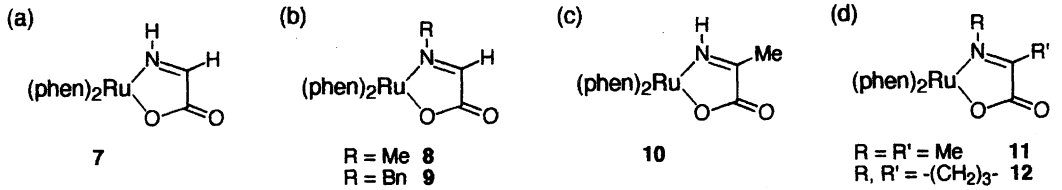


Fig. 1. The change of the UV/visible spectrum of the glycinato complex [Ru(gly)(phen)$_2$]$^+$ **1** with the addition of CAN by 0.25 equivalent amount.



Scheme 1.

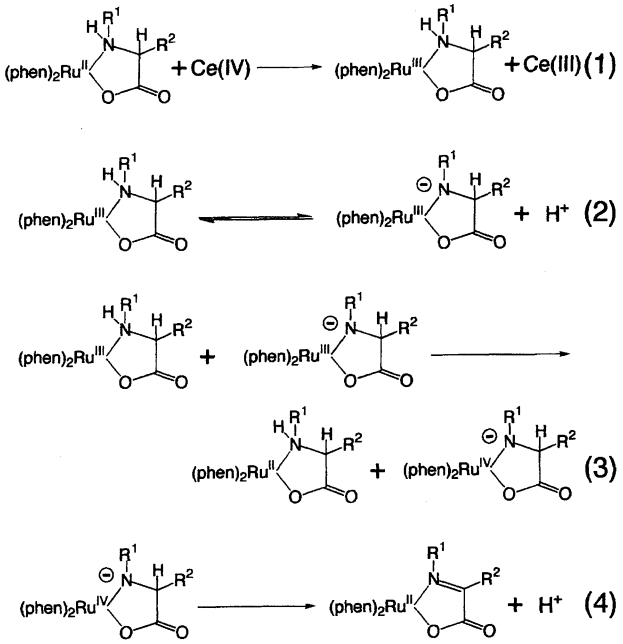


Scheme 2.

N-substituent and/or *C*-substituent. Every type of the typical (α-imino acidato)ruthenium(II) complexes **7**—**12** were obtained by oxidation of the α-amino acidato complexes using CAN (Scheme 2). The iminoacetatoruthenium(II) complex ($[Ru(NH{=}CHCO_2)(phen)_2]^+$) was synthesized for the first time using CAN.[17]

Although we have not yet carried out an extensive mechanistic study, the reaction mechanism may be assumed by analogy with those for the dehydrogenation of the amine ruthenium complexes proposed by Keene and coworkers,[21] and of the hexaamine cage complex by Sargeson and Bernhard,[15b] as follows: The first step is one-electron oxidation by the Ce(IV) ion from Ru(II) to Ru(III) (Scheme 3(1)).[22,23] The next step is proton dissociation of the amino group (Scheme 3(2)); then, disproportionation between two Ru(III) species yields the original Ru(II) complex and the Ru(IV) intermediate (Scheme 3(3)). A proton is removed from the Ru(IV) intermediate, and the (α-imino acidato)ruthenium(II) complex is then produced. The overall reaction is two-electron oxidation. In the case of the dehydrogenation of the amine osmium(II) complex, the Os(IV) species, which was the intermediate of the disproportionation of the Os(III) species, was isolated and the molecular structure of that was determined by an X-ray crystallographic analysis.[20] As for the dehydrogenation of the amine ruthenium(II) complex, the production of the Ru(IV) species, the intermediate of the disproportionation of the Ru(III) species, was detected by means of the UV/visible spectrum.[15] The absorption spectrum of the intermediate resembles that of the Os(IV) species.

The oxidized products, which were identified as the (α-imino acidato)ruthenium(II) complexes $[Ru^{II}\{N(R^1){=}C(R^2)\text{-}CO_2\}(phen)_2]^+$ (R^1 = H, Me, or Bn, R^2 = H; R^1 = H, or Me, R^2 = Me; R^1, R^2 = $-(CH_2)_3-$; X = Cl, ClO_4 or PF_6), were isolated as the chloride, perchlorate or hexafluorophosphate salt in 57—87% yield. The ruthenium complex ions were observed by fast atom bombardment mass spectrometry, and the isotope distribution of the ions is in good agreement with the calculated value. For instance, the *m/z* value of the glycinato complex is 536; on the other hand, that of the oxidized product is 534. Thus, the *m/z* value of the oxidized product is less than that of the starting compound by *two*, which clearly proves that dehydrogenation takes place in the



Scheme 3.

oxidation of the α-amino acidato complexes. The absorption maximum of the electronic spectrum of the α-imino acidato complex in the visible region shows a blue shift of about 30 nm compared to that of the α-amino acidato complex. The shift may reflect a back donation from the ruthenium metal center to the C=N double bond.

The cyclic voltammogram (CV) of the α-amino acidato complexes in 1.0 mol dm^{-3} HCl shows two anodic peaks and a cathodic peak, as shown in Fig. 2(a) for **2**; the data are listed in Table 1. An irreversible anodic peak at 0.55—0.65 V for the α-amino acidato complexes is considered to be a one-electron oxidation of the Ru(II) center to Ru(III). On the other hand, a quasi-reversible couple was observed at about 0.75 V for the α-amino acidato complexes, except for the glycinato and (*S*)-alaninato complexes (**1**, **4**), which is attributed to the product oxidized by the EC reaction. The cyclic voltammograms of the α-imino acidato complexes display a reversible couple, as shown in Table 1, which is identical to those observed with the α-amino acidato complexes. The half-wave potential (about 0.75 V) of the α-

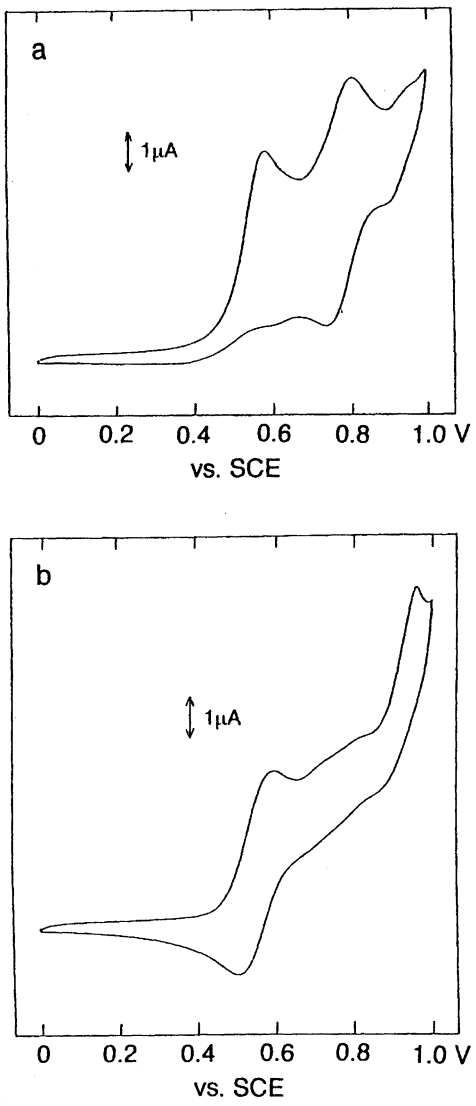


Fig. 2. Cyclic voltammograms of (a) [Ru(*N*-Me-gly)-(phen)$_2$]$^+$ **2** and (b) [Ru(gly)(phen)$_2$]$^+$ **1** in 1.0 mol dm^{-3}HCl (Pt working electrode; scan rate 50 mV s^{-1}).

imino acidato complex is about 0.2 V more positive than the anodic potential of the corresponding α-amino acidato complex. However, the CVs of the glycinato complex **1** (Fig. 2(b)) and the (*S*)-alaninato complex **4** are different from those of the other α-amino acidato complexes, and the CVs of the iminoacetato (NH=CHCO$_2^-$) complex **7** and 2-iminopropionato (NH=C(CH$_3$)CO$_2^-$) complex **10** show two irreversible anodic peaks. Although a pseudo-reversible peak was observed at 0.59 V for **1** and **4**, the reversible peak of the corresponding α-imino acidato complexes was not observed. These results suggest that electrolysis at a constant potential of the glycinato and the (*S*)-alaninato complexes may be difficult to yield the corresponding α-imino acidato complexes because of further oxidation of the product. In fact, no α-imino acidato complex was obtained by electrolysis at a constant potential of the glycinato and the (*S*)-alaninato complexes. It thus appears that electrolysis at a constant potential is unsuitable to dehydrogenate α-amino acidato complexes having no *N*-substituent. On the other hand, oxidation using CAN as the oxidizing reagent is capable of dehydrogenating α-amino acidato complexes, even with no *N*-substituent, such as the glycinato complex, to give the corresponding α-imino acidato complexes.

Table 1. Anodic and Cathodic Peaks of Amino and Imino Acidato Complexes[a)]

[Ru(L)(phen)$_2$]$^+$ L		Anodic peak E_a/V		Cathodic peak E_c/V
gly	**1**	0.59		0.51
N-Me-gly	**2**	0.58	0.81	0.74
N-Bn-gly	**3**	0.65	0.82	0.76
(*S*)-ala	**4**	0.59	0.78	0.51
N-Me-(*S*)-ala	**5**[b)]	0.59	0.74	0.69
(*S*)-pro	**6**[b)]	0.55	0.78	0.72
gly-H$_2$	**7**	0.65	0.80	
N-Me-gly-H$_2$	**8**		0.81	0.74
N-Bn-gly-H$_2$	**9**		0.83	0.76
ala-H$_2$	**10**	0.71	0.90	0.83
N-Me-ala-H$_2$	**11**[b)]		0.75	0.69
pro-H$_2$	**12**[b)]		0.78	0.72

a) Scan rate 50 mV s^{-1}; potentials vs. SCE; Pt electrode; in 1.0 mol dm^{-3}HCl. b) Ref. 8.

The ^{1}H and ^{13}C NMR spectra of the α-imino acidato complexes are consistent with the proposed structures. The ^{1}H NMR spectrum of the α-imino acidato complex derived from the *N*-methylglycinato complex exhibits downfield shifts of the *N*-methyl group (0.83 and 1.60 ppm from the isomer I and II) compared to those of the *N*-methylglycinato complex. In case of the (*S*)-alaninato complex, downfield shifts of the *C*-methyl group (0.75 and 0.91 ppm) of the ala-H$_2$ complex compared to those of (*S*)-alaninato complex were observed. These downfield shifts were similar to those observed with the α-amino acidato cobalt(III) complexes[3,5)] and the *N*-methylalaninato ruthenium(II) complexes.[8)] Although the peak of the imino(N=C*H*) proton of the methyliminoacetato (Me–N=C*H*CO$_2$) complex overlaps those of the aromatic protons of the phenanthrolines, the peak at 8.1 ppm (in CD$_3$OD) is assigned as the imino proton by the measurement of HH COSY spectrum, because the ^4J coupling was observed between the imino proton and the *N*-methyl protons (Fig. 3). Similarly, the peak of the imino proton of *N*-benzyliminoacetato (Bn–N=C*H*CO$_2$) was observed at 8.48 ppm. As for ^{13}C NMR spectra, it is generally difficult to distinguish the peak of *C*=N carbon from that of *C*=O carbon of the α-imino acidato complex having a *C*-substiuent on the imino group. However, in the case of the α-imino acidato complex of the glycine derivative, which has no *C*-substituent on the imino group, the peaks of the *C*=N carbon can be easily assigned by the DEPT method. The ^{13}C NMR spectrum of the methyliminoacetato (Me–N=CHCO$_2$) ruthenium(II) complex display two peaks at 171—180 ppm; a peak resonated at a higher magnetic field was assigned as the *C*=N carbon by the DEPT spectrum measurement, as shown in Fig. 4.

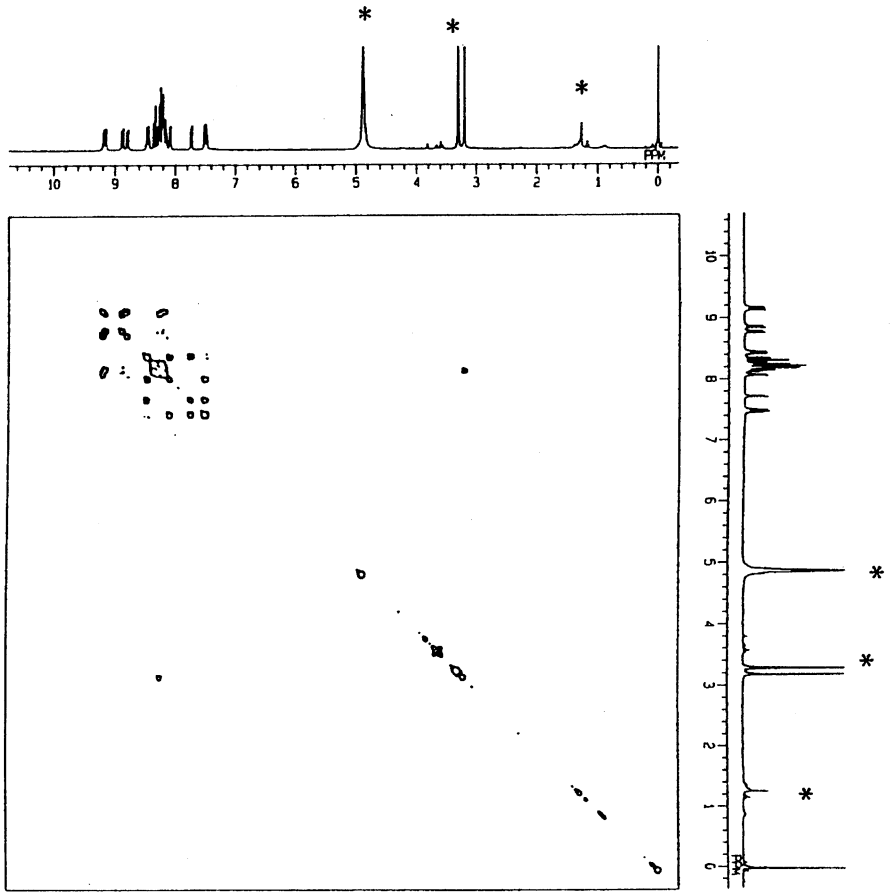


Fig. 3. HH COSY spectrum of the methyliminoacetato complex [Ru(*N*-Me-gly-H_2)(phen)$_2$]$^+$ **8** (270 MHz, in CD_3OD). The peaks with asterisk are those of solvent or impurities.

In conclusion, all four possible types of the (α-imino acidato)ruthenium(II) complexes with or without *N*- and/or *C*-substituent(s) were obtained from the corresponding (α-amino acidato)ruthenium(II) complexes by chemical oxidation using diammonium cerium(IV) nitrate (CAN) as the oxidizing reagent. In particular, the iminoacetatoruthenium-(II) complex [Ru(NH=$CHCO_2$)(phen)$_2$]$^+$ (**7**), of which the α-imino acidato moiety is the simplest one with no substituent on the imino group, was synthesized for the first time by this method.[17] The dehydrogenation of the (α-amino acidato)-ruthenium(II) complexes with CAN is more facile and versatile than any other method that we have ever examined, including hydrogen peroxide.

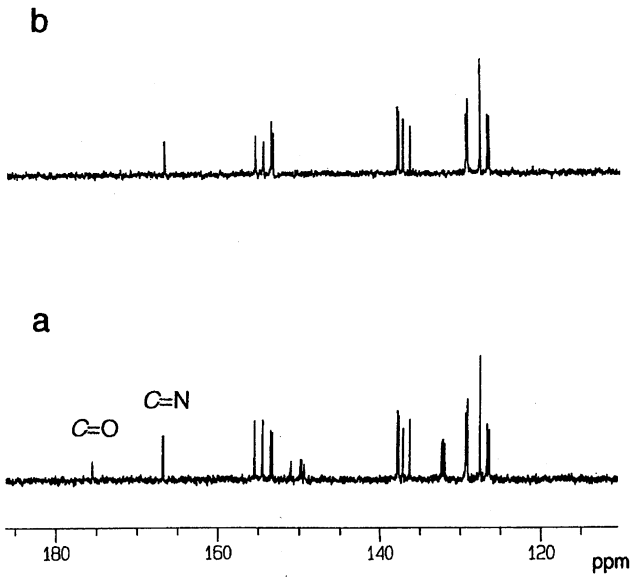


Fig. 4. (a) ^{13}C NMR and (b) DEPT 90° (CH) spectra of [Ru(*N*-Me-gly-H_2)(phen)$_2$]$^+$ **8** (67.5 MHz, in CD_3OD).

The authors are grateful to Prof. Tomomichi Ishikawa and Dr. Takehiko Suzuki for use of the instrument for elemental analyses.

References

1) A part of this study has been presented at "the 30th International Conference on Coordination Chemistry," M. Yamaguchi, T. Mori, and T. Yamagishi, Kyoto, Japan, July 1994, Abstr., S2-41.

2) K. J. Drok, J. M. Harrowfield, S. J. McNiven, A. M. Sargeson, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, **46**, 1557 (1993), and references cited therein.

3) a) M. Yamaguchi, M. Saburi, and S. Yoshikawa, *J. Am. Chem. Soc.*, **106**, 8293 (1984); b) M. Yamaguchi, M. Saburi, S. Yoshikawa, and T. Yamagishi, *Bull. Chem. Soc. Jpn.*, **67**, 1341

(1994).

4) a) J. M. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 2634 (1974); b) J. M. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc.*, **101**, 1514 (1979).

5) a) A. Hammershøi, R. M. Hartshorn, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, **1988**, 1226; b) A. Hammershøi, R. M. Hartshorn, and A. M. Sargeson, *Inorg. Chem.*, **29**, 4525 (1990); c) R. M. Hartshorn and A. M. Sargeson, *Aust. J. Chem.*, **45**, 5 (1992).

6) E. K. Chong, J. M. Harrowfield, W. G. Jackson, A. M. Sargeson, and J. Springborg, *J. Am. Chem. Soc.*, **107**, 2015 (1985).

7) a) M. Yamaguchi, T. Yamagishi, and M. Hida, "36th Symposium on Coordination Chemistry," Nagoya, Japan, Oct. 1986, Abstr., No. 3A10; b) M. Yashiro, S. Miura, T. Matsuyama, S. Yoshikawa, M. Komiyama, and S. Yano, *Inorg.Chem.*, **33**, 1003 (1994).

8) a) M. Yamaguchi and T. Yamagishi, *Inorg. Chem.*, **32**, 2981 (1993); b) M. Yamaguchi, K. Machiguchi, T. Mori, K. Kikuchi, I. Ikemoto, and T. Yamagishi, *Inorg. Chem.*, **35**, 143 (1996), and references cited therein.

9) J. Meder, W. Petri, and W. Beck, *Chem. Ber.*, **117**, 827 (1984).

10) B. Wagner, U. Taubald, and W. Beck, *Chem. Ber.*, **122**, 1031 (1989).

11) Preliminary experiment showed that the α-imino acidato Ru(II) complex reacts with nucleophilic reagent. Sodium borohydride was added to an aqueous solution of [Ru(*N*-Bn-gly-H_2)(phen)$_2$]Cl, and the mixture was stirred for 24 h at room temperature. The corresponding α-amino acidato complex, [Ru(*N*-Bn-gly)(phen)$_2$]Cl, was obtained (yield: 89%): T. Mori, M. Yamaguchi, and T. Yamagishi, unpublished results.

12) T. Mori, M. Yamaguchi, and T. Yamagishi, unpublished results.

13) a) B. C. Lane, J. E. Lester, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, **1971**, 1618; b) D. F. Mahoney and J. K. Beattie, *Inorg. Chem.*, **12**, 2561 (1973); c) S. E. Diamond, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **97**, 2661 (1975).

14) a) G. M. Brown, T. R. Weaver, F. R. Keene, and T. J. Meyer, *Inorg. Chem.*, **15**, 190 (1976); b) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **98**, 1884 (1976); c) P. A. Adcock, F. R. Keene, R. S. Smythe, and M. R. Snow, *Inorg. Chem.*, **23**, 2336 (1984); d) G. W. Whebell and F. R. Keene, *Aust. J. Chem.*, **39**, 2027 (1986).

15) a) P. Berhard, A. M. Sargeson, and F. C. Anson, *Inorg. Chem.*, **27**, 2754 (1988); b) P. Berhard and A. M. Sargeson, *J. Am. Chem. Soc.*, **111**, 597 (1989).

16) T. -L. Ho, *Synthesis*, **1973**, 347.

17) Recently, the synthesis of the iminoacetatocobalt(III) complex by the oxidation of the glycinato complex using NBS and PBr_3 has been reported: L. Bendahl, A. Hammershøi, D. Kjærgaard Jensen, E. Kaifer, A. M. Sargeson, and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, **1996**, 1649.

18) P. A. Lay, A. M. Sargeson, and H. Taube, *Inorg. Synth.*, **24**, 291 (1986).

19) R. Vagg and P. A. Williams, *Inorg. Chim. Acta*, **58**, 101 (1982).

20) P. A. Lay, A. M. Sargeson, B. W. Skelton, and A. H. White, *J. Am. Chem. Soc.*, **104**, 6161 (1982).

21) a) M. J. Ridd and F. R. Keene, *J. Am. Chem. Soc.*, **103**, 5733 (1981); b) F. R. Keene, M. J. Ridd, and M. R. Snow, *J. Am. Chem. Soc.*, **105**, 7075 (1983).

22) The mechanism of the dehydrogenation of the amine Fe(III) complexes proposed by Goto and co-workers does not involve the Fe(IV) intermediate, but the electron of the deprotonated amino nitrogen of the Fe(III) species was transferred intramolecularly to the iron center to give the Fe(II) intermediate.[23]

23) a) A. M. da Costa Ferreira and H. E. Toma, *J. Chem. Soc., Dalton Trans.*, **1983**, 2051; b) M. Goto, M. Takeshita, N. Kanda, T. Sakai, and V. L. Goedken, *Inorg. Chem.*, **24**, 582 (1985); c) Y. Kuroda, N. Tanaka, M. Goto, and T. Sakai, *Inorg. Chem.*, **28**, 2163 (1989).