Dalton Transactions

Formation of Bis(2-pyridylcarbonyl)aminate by Oxidation of Ethylbis(2-pyridylmethyl)amine on Trichloridoruthenium(III) Complex

Journal:	*Dalton Transactions*
Manuscript ID:	DT-ART-06-2014-001842.R2
Article Type:	Paper
Date Submitted by the Author:	16-Aug-2014
Complete List of Authors:	Nagao, Hirotaka; Sophia University, Department of Materials and Life Sciences Shimura, Naoto; Sophia university, Yonezawa, Haruka; Sophia university,

Dalton Transactions RSCPublishing

ARTICLE

Formation of Bis(2-pyridylcarbonyl)aminate by Oxidation of Ethylbis(2-pyridylmethyl)amine on Trichloridoruthenium(III) Complex

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hirotaka Nagao*, Naoto Shimura, and Haruka Yonezawa

Oxidation of the *facial*-type trichloridoruthenium(III) complex bearing ethylbis(2-pyridylmethyl)amine (ebpma), *fac*-[$Ru^{III}Cl_3$(ebpma)], with equimolecular amount of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ in acetonitrile afforded a ligand-base oxidation product of an acetonitriledichloridoruthenium(III) complex having bis(2-pyridylcarbonyl)aminato (bpca), [$Ru^{III}Cl_2(NCCH_3)$(bpca)]. The complex changed into trichloridorutheniun(III) complex by a reaction with hydrochloric acid and triacetonitrileruthenium(II) complex by reduction with Zn in ethanol-acetonitrile. The bpca moiety showed interaction with cations such as proton.

Introduction

Redox reactions of metal complexes are important tools for synthesis of new metal complexes and development of their properties. Metal complexes have been widely investigated in connection with applications toward conversion reactions of materials and organic syntheses.[1,2] Activation and conversion reactions of stable molecules to valuable compounds have been studied using redox reactions of metal complexes. Recently, reactions of metal complexes, where both the metal centre and ligands function cooperatively in conversion of compounds, have been developed.[2] Metal complexes having amine groups have received attention as useful nitrogen sources in synthesis of nitrogen-containing compounds. Oxidation reactions of amines by oxygen-containing oxidant afford hydroxylamine, nitroso, and nitro compounds in addition to imine and iminium moieties.[3-7] Amine moieties coordinated to metal complexes were oxidized to afford corresponding imine, nitrile, amide, and nitrogen-containing compounds by oxidation of metal complexes. Cooperative reactions with both the metal centre and the ligand have been reported in reactions using ruthenium complexes having a tridentate PNP or PNN-type pincer ligand.[7-14]

Ruthenium complexes bearing a tridentate ethylbis(2-pyridylethyl)amine (ebpea), which can coordinate in both facial and meridional configurations around the metal centre with two pyridyl and one amine nitrogen atoms, showed redox induced reactions at the ebpea ligand.[15,16] The amine group and the ethylene-chain, which connects between the amine and pyridyl groups of the ebpea ligand, cooperated with the ruthenium centre or the coexisting ligand such as NO ligand to give the imine moiety, Ru{η^2-N(Et)(C_2H_4py)=$CHCH_2$py}, and the nitroso moiety, Ru{N(O)CH(py)CH_2N(Et)(C_2H_4py)}, that were formed via C-H activation of the ethylene-chain of the ebpea ligand. These reactions indicate that the geometrical configuration of the ebpea ligand around the ruthenium centre relates to their reactivity. In this study, bis(2-pyridylcarbonyl)aminate (bpca), as shown in Fig. 1, was formed from ethylbis(2-pyridylmethyl)amine (ebpma) on the trichloridoruthenium(III) complex, *fac*-[$Ru^{III}Cl_3$(ebpma)], by an one-electron oxidation reaction using equimolecular amounts of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (CAN) in CH_3CN. The bpca ligand and the related aminato ligands have been previously synthesized by hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine mediated with metal complexes[18-21] and organic syntheses or conversion of organic compounds on metal complexes.[22-24] Accumulation and magnetic properties of metal complexes bearing bpca have been reported in connection with magnetic interaction between metal centres.[25-32] The present bpca complex of ruthenium(III) containing one acetonitrile and two chlorido ligands was formulated as [$Ru^{III}Cl_2(NCCH_3)$(bpca)]. This Ru(III) complex changed into a trichlorido complex of Ru(III), [$Ru^{III}Cl_3$(Hbpca)], by a ligand-substitution reaction and was reduced by zinc in ethanol-acetonitrile to give a corresponding triacetonitrile complex of Ru(II), [$Ru^{II}(NCCH_3)_3$(bpca)]PF_6. Structures of these complexes were characterized by X-ray crystallography. Interaction between the bpca moiety and mono-cation such as proton, lithium and sodium ions were observed by cyclic voltammetry.

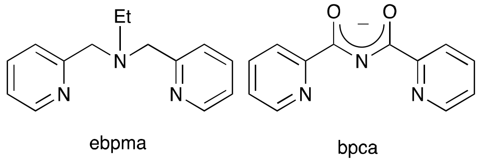


Fig. 1 Structures of ethylbis(2-pyridylmethyl)amine (ebpma) and bis(2-pyridylcarbonyl)aminate (bpca).

Table 1 Crystallographic data for $[Ru^{III}Cl_2(NCCH_3)(bpca)]\cdot CH_3CN$, $[Ru^{III}Cl_3(Hbpca)]\cdot 4.5H_2O$ and $[Ru^{II}(NCCH_3)_3(bpca)]PF_6\cdot 1.25H_2O$

	$[Ru^{III}Cl_2(NCCH_3)(bpca)]\cdot CH_3CN$	$[Ru^{III}Cl_3(Hbpca)]\cdot 4.5H_2O$	$[Ru^{II}(NCCH_3)_3(bpca)]PF_6\cdot 1.25H_2O$
Formula	$C_{16}H_{14}N_5O_2Cl_2Ru$	$C_{12}H_{18}N_3O_{6.5}Cl_3Ru$	$C_{18}H_{19.5}F_6N_6O_{3.25}PRu$
*F*w	480.29	515.72	617.92
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	$P2_1/n$	*P*-1
a/Å	8.554(3)	10.139(4)	8.838(3)
b/Å	10.187(3)	8.711(4)	11.366(4)
c/Å	11.190(3)	21.250(8)	13.810(5)
α/°	73.047(7)	90	70.735(15)
β/°	89.624(10)	96.7949(15)	71.344(13)
γ/°	85.182(9)	90	70.709(16)
V/Å^3	929.3(5)	1863.6(12)	1201.0(7)
Z	2	4	2
μ/cm^{-1}	11.52	13.07	8.00
T/K	93	93	93
d_{calcd}/g cm$_{-3}$	1.716	1.838	1.709
No of obsd. refls ($I > 2\sigma(I)$)	5909	14104	11904
No of unique refs (R_{int})	3209(0.0139)	4265(0.0267)	5384 (0.0134)
No of parameters	309	253	333
GOF	1.064	1.117	1.028
R_1	0.0218	0.0352	0.0212
wR_2	0.0519	0.0794	0.0538

Experimental

General procedures

$RuCl_3\cdot nH_2O$ (content of Ru: 40.46 wt%) was purchased from Furuya Kinzoku Inc. All solvents and chemicals were purchased as dehydrated grade and reagent grade, respectively, and were used without further purification. Ethylbis(2-pyridylmethyl)amine (ebpma) was prepared by the procedure reported in the literature.[33] All complexes were synthesized under air. *fac*-$[Ru^{III}Cl_3(ebpma)]$ was synthesized according to the previously reported procedure.[34] IR spectra were recorded on a Shimazu IR Affinity-1 spectrophotometer using samples prepared as KBr disks. UV-vis spectra in CH_3CN were recorded on a Shimadzu MultiSpec-1500. ^1H and ^{13}C NMR spectra in CD_3CN were recorded on a JEOL AL-500 spectrometer. The effective magnetic moment was measured by the Guy method using $Hg[Co(SCN)_4]$ as a calibrant at 300 K. Electrochemical measurements such as cyclic voltammograms (CVs), normal pulse voltammograms (NPVs), and differential pulse voltammograms (DPVs) were carried out on acetonitrile solutions containing 0.10 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as supporting electrolyte using Pt disk working electrode (ϕ = 1.6 mm) and Ag| 0.01 mol dm^{-3} $AgNO_3$ (CH_3CN) reference electrode using a BAS 100B/W electrochemical analyzer at room temperature and -40°C. Hydrodynamic voltammograms (HDVs) were obtained with a rotating platinum-disk working electrode (ϕ = 3.0 mm) using a BAS RDE-2 rotating electrode. Controlled potential electrolysis (CPE) experiments were carried out in a three-compartment cell with a platinum gauze working electrode in the first-compartment, an auxiliary electrode in the second-compartment, and an reference electrode in the third-compartment using a Huso polarograph Model 312 and 343B digital coulometer. At the end of each measurement, ferrocene was added as an internal standard to correct redox potentials.

Synthesis of $[Ru^{III}Cl_2(NCCH_3)(bpca)]\cdot H_2O$

A CH_3CN solution of *fac*-$[Ru^{III}Cl_3(ebpma)]$ (50 mg, 0.12 mmol) with $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (63 mg, 0.12 mmol) was refluxed for 5 hrs to give a red solution. To isolate a brown complex, the volume of the solution was reduced until *ca.* 3 cm^3 and H_2O was added to afford the brown complex as a powder. The obtained brown powder was collected by filtration and washed with H_2O, C_2H_5OH, and ether (20 mg, 36%). Elemental analysis. Calcd for $C_{14}H_{13}N_4O_3Cl_2Ru$: C 36.77, H 2.87, N 12.25%. Found: C 36.76, H 2.82, N 12.28%. FAB MS: 440($RuCl_2(NCCH_3)(bpca) + H^+$), 399($RuCl_2(bpca) + H^+$), and 363(RuCl(bpca)). The magnetic moment of the brown complex in the solid state is 1.82 μ_B. The same complex was also obtained by the reaction of the similar trichloridoruthenium(III) complex bearing benzylbis(2-pyridylethyl)amine (bbpma). In the reaction of bbpma complex, formation of benzaldehyde was confirmed by gas chromatography on a GL-Science GC-4000 with a capillary column and ^1H NMR spectroscopy of the reaction mixture.

Synthesis of $[Ru^{III}Cl_3(Hbpca)]\cdot 4H_2O$

A suspended solution of $[Ru^{III}Cl_2(NCCH_3)(bpca)]\cdot H_2O$ (60 mg, 0.13 mmol) in H_2O (47 cm^3) containing hydrochloric acid (37%, 3 cm^3) was refluxed for 3 hrs to give a yellow solution. The volume of the yellow solution was reduced to *ca.* 10 cm^3. After cooling the solution in refrigerator, the formed yellow powder was collected by filtration and washed with H_2O (38 mg, 67%). Elemental analysis. Calcd for $C_{12}H_{17}N_3O_6Cl_3Ru$: C 28.44, H 3.38, N 8.29%. Found: C 28.50, H 3.54, N 8.25%. FAB MS(+): 399($RuCl_2(Hbpca)$) and 363(RuCl(Hbpca)). FAB MS(-): 435($RuCl_3(bpca)$). The magnetic moment in the solid state is 1.88 μ_B.

Synthesis of [$Ru^{II}(NCCH_3)_3(bpca)$]$PF_6 \cdot 1.25H_2O$

[$Ru^{III}Cl_2(NCCH_3)(bpca)$]$\cdot H_2O$ (60 mg, 0.13 mmol), was reduced by zinc powder in C_2H_5OH-CH_3CN (2:1, 15 cm^3) under stirring conditions for 24 hrs to give a red solution. After removing Zn, the red solution was allowed to stand for 24 hrs. The red complex was obtained from the red solution after reducing the volume of the solution and addition of an ethanoic solution containing NH_4PF_6 as a precipitant. The obtained red complex was collected by filtration and washed with H_2O, C_2H_5OH, and ether (25 mg, 32%). The red complex was purified by column chromatography using SP-Sephadex with $(CH_3)_2CO$-CH_3CN (1:1, *v*/*v*) as eluent. The obtained red powder was recrystallized from CH_3CN-H_2O by slow-evaporation to give red crystalline complexes. Elemental analysis. Calcd for $C_{18}H_{19.5}N_6O_{3.25}F_6PRu$: C 34.99, H 3.18, N 13.60%. Found: C 35.20, H 3.02, N 13.16%. FAB MS: 451($Ru(NCCH_3)_3(bpca)$), 410($Ru(NCCH_3)_2(bpca)$), 369($Ru(NCCH_3)(bpca)$), and 328(Ru(bpca)). ^1H NMR (500 MHz, CD_3CN, TMS): δ 2.05 (s, 6H, CH_3CN), 2.65 (s, 3H, CH_3CN), 7.69 (m, 2H, py(bpca)), 8.08 (m, 2H, py(bpca)), 8.14 (m, 2H, py(bpca)), 8.91 (d, 2H, py(bpca)). ^{13}C NMR (126 MHz, CD_3CN, TMS): δ 3.9 ($\mathit{C}H_3CN$), 4.4 ($\mathit{C}H_3CN$), 124.3 ($CH_3\mathit{C}N$), 125.2 ($CH_3\mathit{C}N$), 127.4, 128.8, 138.6, 154.6, 154.7, 159.7, 171.0 (bpca).

X-ray crystallography

Single crystal of [$Ru^{III}Cl_2(NCCH_3)(bpca)$]$\cdot CH_3CN$ was obtained by recrystallization from CH_3CN using vapor diffusion of ether and those of [$Ru^{III}Cl_3(Hbpca)$]$\cdot 4.5H_2O$ and [$Ru^{II}(NCCH_3)_3(bpca)$]$PF_6 \cdot 1.25H_2O$ were obtained by slow-evaporation from H_2O and CH_3CN-H_2O, respectively. Intensity data were collected on a Rigaku Mercury CCD diffractometer, using graphite-monochromated MoKα radiation (0.71069 Å). All the calculations were carried out using the Crystal Structure software package (Crystal Structure 4.0, Single Crystal Structure Analysis Software). Structures were solved by direct methods, expanded using Fourier techniques, and refined using full-matrix least-square techniques on F^2 using SHELXL97. Crystallographic data were summarized in Table 1. Further information on the crystal structure determination (excluding structure factors) has been deposited in the Cambridge Crystallographic Data Center as supplementary publications no. CCDC 1008877 for [$Ru^{III}Cl_2(NCCH_3)(bpca)$]$\cdot H_2O$, CCDC 892552 for [$Ru^{II}(NCCH_3)_3(bpca)$]$PF_6 \cdot 1.25H_2O$ and CCDC 1008878 for [$Ru^{III}Cl_3(Hbpca)$]$\cdot 4.5H_2O$.

Results and discussion

Oxidation of *fac*-[$Ru^{III}Cl_3(ebpma)$]

The CV of *fac*-[$Ru^{III}Cl_3(ebpma)$] in CH_3CN at room temperature showed irreversible reduction and oxidation waves at -0.56 and 1.01 V, respectively, as shown Fig. 2(a).[34] In the CV at -40°C (see Fig. S1(b) in the Supplementary Information), these waves were observed as reversible waves. The oxidation wave was confirmed as a Nernstian one-electron process by analysis of NPV (see Fig. S2 in the Supplementary Information) assigning to a couple between Ru^{III} and Ru^{IV}. The irreversible oxidation at room temperature within the time scale of cyclic voltammetry and the controlled potential electrolysis (CPE) of *fac*-[$Ru^{III}Cl_3(ebpma)$] afforded a new complex, showing an irreversible oxidation wave around 1.2 V (see Fig. S1(c) in the Supplementary Information). Thus, the one-electron oxidized complex is unstable and immediately changes in CH_3CN.

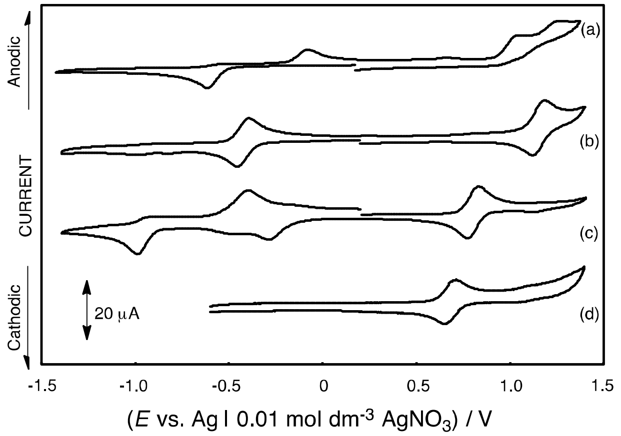


Fig. 2 CVs of ruthenium complexes (1.0 mmol dm^{-3}) in CH_3CN containing 0.10 mol dm^{-3} TEAP at 25°C with scan rate 100 mV s^{-1}; (a) *fac*-[$Ru^{III}Cl_3(ebpma)$], (b) [$Ru^{III}Cl_2(NCCH_3)(bpca)$], (c) [$Ru^{III}Cl_3(Hbpca)$] and (d) [$Ru^{II}(NCCH_3)_3(bpca)$]$PF_6$.

The CH_3CN solution of *fac*-[$Ru^{III}Cl_3(ebpma)$] containing equimolecular amounts of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (CAN) was refluxed under air until the colour of the solution changed to red. The formed complex was isolated as a mono hydrate complex, [$RuCl_2(NCCH_3)(bpca)$]$\cdot H_2O$. By addition of $NaClO_4$ or NH_4PF_6 to the red solution, [$RuCl_2(NCCH_3)(bpca)$]$\cdot$-*n*$NaClO_4$ or [$RuCl_2(NCCH_3)(bpca)$]$\cdot$*n*NH_4PF_6 precipitated. Solubility of the hydrated complex in CH_3CN was slightly lower than those of $NaClO_4$ and NH_4PF_6-adducts. The structure of the complex [$RuCl_2(NCCH_3)(bpca)$]$\cdot CH_3CN$, which was recrystallized from CH_3CN, was determined by X-ray crystallography. The ebpma ligand changed into bis(2-pyridylcarbonyl)aminate (bpca) coordinated to the Ru(III) centre with two pyridyl and one aminate nitrogen atoms. The FAB MS spectrum reveals a molecular ion peak at *m*/*z* 440 for $\{RuCl_2(NCCH_3)(bpca) + H^+\}^+$, and two fragment peaks due to loss of acetonitrile and/or chlorido ligands at *m*/*z* 399 for $\{RuCl_2(bpca) + H^+\}^+$ and 363 for $\{RuCl(bpca)\}^+$. The effective magnetic moment of 1.82 μ_B at room temperature supported its characterization as a Ru(III) complex. Properties of the complexes were summarized in Table 2. In the IR spectrum of a KBr disk, a new strong absorption band was observed at 1719 cm^{-1} (see Fig. S3(b) in the Supplementary Information) and was assigned to a stretching C=O vibrational of the aminato moieties. These results indicate that the brown complex is characterized as an acetonitriledichlorido complex of ruthenium(III) bearing the bis(2-pyridylcarbonyl)aminato ligand (bpca in Fig. 1), [$Ru^{III}Cl_2(NCCH_3)(bpca)$], where the

Table 2 Properties and structural parameters of complexes

complex	$[Ru^{III}Cl_2(NCCH_3)(bpca)]\cdot CH_3CN$			$[Ru^{III}Cl_3(Hbpca)]\cdot 4.5H_2O$			$[Ru^{II}(NCCH_3)_3(bpca)]PF_6\cdot 1.25H_2O$		
ν(C=O) / cm^{-1}	1719			1714			1696		
$E(Ru^{IV}/Ru^{III})$ / V	1.17			0.79					
$E(Ru^{III}/Ru^{II})$ / V	-0.41			-0.31[a]	-0.94[a]		0.68		
λ / nm	264	371		264	370	429	225	370	
(ε / mol^{-1} dm^3 cm^{-1})	(11700)	(6750)		(14100)	(7820)	(2600)	(24400)	(7700)	
Ru-N_1(aminato)	1.962(2)			1.976(3)			2.0197(16)		
Ru-N(pyridyl)	2.062(2)	2.0572(19)		2.061(3)	2.058(3)		2.0679(15)	2.0647(14)	
Ru-X trans to N(aminato)	X = N			X = Cl			X = N		
	2.091(3)			2.3921(12)			2.0564(16)		
trans to Y	Y = Cl			Y = Cl			Y = N		
	2.3469(9)	2.3365(9)		2.3656(11)	2.3543(11)		2.0212(16)	2.0199(16)	
N_1(aminato)-C(carbonyl)	1.393(3)	1.379(3)		1.373(4)	1.378(4)		1.368(3)	1.3683(18)	
C(carbonyl)-O	1.209(4)	1.216(4)		1.223(4)	1.221(4)		1.226(3)	1.225(2)	
C(carbonyl)-C(pyridyl)	1.511(4)	1.509(4)		1.502(5)	1.501(5)		1.514(2)	1.516(3)	
N_1(aminato)-Ru-N(pyridyl)	82.02(8)	81.52(8)		81.66(10)	81.66(11)		80.78(6)	80.65(6)	
X-Ru-Y, Y-Ru-Y	88.48(6)	87.28(6)	175.64(3)	89.43(3)	91.54(6)	178.92(3)	89.64(6)	90.60(6)	178.43(5)
Ru-N_1(aminato)-C(carbonyl)	117.36(16)	117.89(16)		116.36(19)	116.9(2)		117.21(10)	117.59(13)	
N_1(aminato)-C(carbonyl)-O	127.3(2)	127.8(3)		126.1(3)	126.0(3)		128.06(14)	128.07(17)	
C(carbonyl)-N_1(aminato)-C(carbonyl)	124.8(2)			126.5(3)			125.08(14)		
N_1(aminato)-C(carbonyl)-C(pyridyl)	111.1(2)	111.0(3)		112.1(3)	112.1(3)		111.81(14)	111.06(14)	

[a] irreversible E_{pc}

bpca ligand is the oxidation product of the ethylbis(2-pyridylmethyl)amine ligand. The formation of the bpca ligand on the ruthenium centre is an unexpected reaction and this formation process of bpca is the first synthetic procedure from alkylamine coordinated to the ruthenium complex. The aminato complex, $[Ru^{III}Cl_2(NCCH_3)(bpca)]$, was also obtained by oxidation using the corresponding *mer*-form ethylbis(2-pyridylmethyl)amine complex, *mer*-$[Ru^{III}Cl_3(ebpma)]$ as a starting complex, whereas the yield of the product was lower than that using the *fac*-form with an unidentified complex. This result indicates that the structural configuration around the Ru centre is important and the *fac*-configuration is favorable for the formation of bpca. To understand the formation process, a similar tridentate supporting ligand, benzylbis(2-pyridylethyl)-amine (bbpma), which was substituted for the ethyl group bound to the amine of ebpma by a benzyl group and coordinated in same manner as ebpma, was used under similar reaction conditions to afford the same product in the same yield. During this reaction, benzaldehyde was formed in *ca.* 80% yields based on the amount of the starting complex. The reaction process is discussed in the latter section.

Reactions of $[Ru^{III}Cl_2(NCCH_3)(bpca)]$

In a reaction of $[Ru^{III}Cl_2(NCCH_3)(bpca)]$ with a Cl^- ion in the presence of hydrochloric acid under refluxing conditions, the substitution for the acetonitrile ligand occurred to afford a yellow complex. This yellow complex shows the strong characteristic CO band at 1714 cm^{-1} in similar to the starting complex, the effective magnetic moment of 1.88 μ_B at room temperature, and the bond distances around the ruthenium centre, indicating the oxidation state of the ruthenium centre is Ru(III). In the light of the results of FAB MS, elemental analysis and electrochemical behaviours, the yellow complex has three chlorido ligands and the neutral tridentate ligand. Complex electrochemical behaviours of the CH_3CN solution as shown in Fig. 2(c) and changes of CV profile were observed by the controlled potential electrolysis (CPE) and addition of $LiOCH_3$ or $NaOCH_3$ to the CH_3CN solution, described in the latter section. In the CPE experiment at -0.6 V, the first irreversible reduction wave disappeared with evolution of H_2. These results indicate that this product is characterized as $[Ru^{III}Cl_3(Hbpca)]$ and a dissociation of a proton from the bpca moiety takes place.

Reduction of $[Ru^{III}Cl_2(NCCH_3)(bpca)]$ in CH_3CN-C_2H_5OH by zinc powder afforded a red solution. A red complex was obtained as a PF_6-salt by addition of NH_4PF_6, and was characterized as a triacetonitrile complex of ruthenium(II), $[Ru^{II}(NCCH_3)_3(bpca)]PF_6$. The IR spectrum of this complex showed a characteristic band at 1696 cm^{-1}, assigned to the CO stretching mode (see Fig. S3(c) in the Supplementary Information), similar to that of $[Ru^{III}Cl_2(NCCH_3)(bpca)]$. The NMR signals in CD_3CN were observed in the normal region, indicating its diamagnetic properties of a Ru(II) complex. The ^1H NMR spectrum showed two signals at 2.65 and 2.05 ppm for two axial CH_3CN ligands and one equatorial CH_3CN coordinated to the ruthenium centre, respectively, and four signals between 7.69 - 8.91 ppm for the pyridyl groups of the bpca ligand (see Fig. S4 in the Supplementary Information). In the ^{13}C NMR spectrum, two pair of signals for methyl at 4.0 and 4.5 ppm and cyano carbon atoms at 124.3 and 125.2 ppm of axial and equatorial CH_3CN ligands, six signals for five pyridyl between 127.5 - 154.7 ppm and carbonyl carbon atoms at 171.1 ppm of the bpca ligand were observed. Electrochemical behaviour in a CH_3CN solution indicated an oxidation wave at 0.68 V, attributed to the Ru(III)/Ru(II) couple (Fig. 2(d)), while no reduction wave was observed within the potential window. The oxidation potential of the aminatoruthenium(II) complex was observed at more negative region than that of the corresponding ebpma complex of Ru(II), due to anionic nature of the aminato ligand.[5]

Structures of bis(2-pyridylcarbonyl)aminato complexes

Single crystals suitable for X-ray crystallography were obtained by recrystallization from CH_3CN or CH_3CN-H_2O mixed solvent, and the structures of three complexes of Ru(III) and Ru(II) were determined. The geometries around the Ru centre of both Ru(II) and Ru(III) complexes are a distorted octahedral with two pyridyl and one aminate groups of the bis(2-pyridylcarbonyl)aminato ligand and three nitrogen or chloride atoms of acetonitrile or chlorido ligands as shown in Fig. 3, 4 and 5. Three acetonitrile and/or chlorido ligands coordinate in a meridional configuration around the ruthenium centre. These complexes were crystalized with solvent molecules and there were interactions between complexes and crystalized molecules. Selected bond distances and angles are summarized in Table 2.

Structural studies on $[Ru^{III}Cl_2(NCCH_3)(bpca)]$ reveal carbonyl moieties of the bpca ligand play an important role in formation of single crystals. Although the suitable single crystals were not obtained, the poor single crystal of the complex precipitated with $NaClO_4$ was obtained and the reasonable crystal structure was determined as $[RuCl_2(NCCH_3)(bpca)]\cdot 0.5NaClO_4$ with strong interactions between Na^+ and Cl^- ligand and O atoms of the bpca ligand (see Fig. S5 in the Supplementary Information). The structural features of the bpca ligand are similar to those of other metal complexes.[20-24,32,35-37] There is a stronger σ-donation of the aminato moiety to the ruthenium centre than amine-type coordination in comparison between the bond distances of the Ru centre and the aminato nitrogen (Ru-N_1(aminato)) and those of the Ru and the pyridyl nitrogen atoms (Ru-N(pyridyl) and Ru-N(amine)) in similar Ru(III) and Ru(II) complexes containing bis(pyridylalkyl)amine such as ebpma and ebpea.[15,16] The difference of the Ru-N_1(aminato) bond distances between Ru(III) and Ru(II) complexes reveals the π-back donation from the Ru centre to the aminato moiety is not important. The structural parameters of the aminato unit, O=C-N-C=O, of the bpca ligand show no significant difference between oxidation states of the Ru centre and protonated or deprotonated of the aminate moiety. The aminato unit and pyridyl groups are sited on the same plane and have a π-conjugated system. The bond distances of Ru-X at the trans position respect toward the aminato moiety were strengthened by the strong σ-donation nature of the aminato moiety. Other Ru-X bond distances of Cl and CH_3CN ligands at the *cis*-positions were usual values for Ru(III) and Ru(II) complexes.

Electrochemical behaviours

CVs and redox potentials of these complexes were summarized in Table 2. These three complexes showed a reversible one-electron oxidation wave at 1.17 V for $[Ru^{III}Cl_2(NCCH_3)(bpca)]$ (Fig. 2(b)), 0.79 V for $[Ru^{III}Cl_3(Hbpca)]$ (Fig. 2(c)) and 0.68 V for $[Ru^{II}(NCCH_3)_3(bpca)]PF_6$ (Fig. 2(d)). The oxidation process for the Ru(III) complexes assigned to the Ru(IV)/Ru(III) couple and that for $[Ru^{II}(NCCH_3)_3(bpca)]PF_6$ to the Ru(III)/Ru(II) couple, respectively. On the reductive scan for $[Ru^{III}Cl_2(NCCH_3)(bpca)]$, a reversible reduction wave was observed at -0.41 V, attributed to the Ru(III)/Ru(II) couple. The CV of $[Ru^{II}(NCCH_3)_3(bpca)]PF_6$ showed no reduction wave within the potential window. At room temperature, $[Ru^{III}Cl_3(Hbpca)]$ exhibited two irreversible reduction waves at

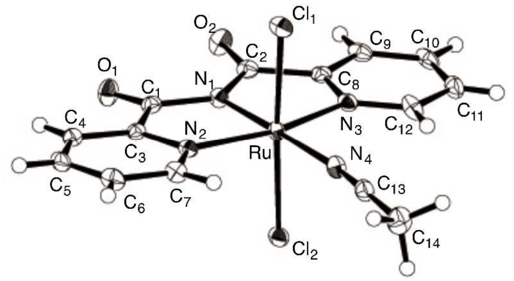


Fig. 3 Structure of $[Ru^{III}Cl_2(NCCH_3)_3(bpca)]$ with thermal ellipsoids at the 50% probability.

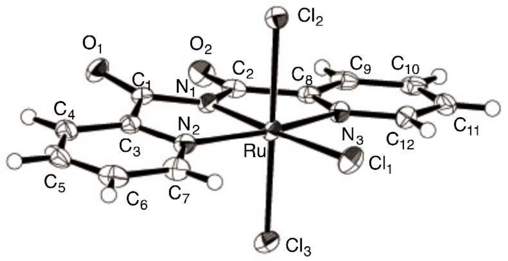


Fig. 4 Structure of $[Ru^{III}Cl_3(Hbpca)]$ with thermal ellipsoids at the 50% probability.

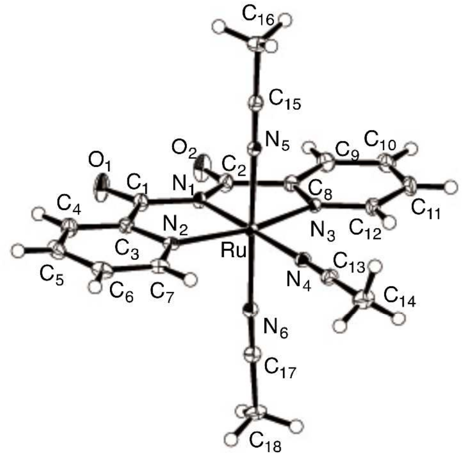


Fig. 5 Structure of $[Ru^{II}(NCCH_3)_3(bpca)]^+$ with thermal ellipsoids at the 50% probability.

-0.31 and -0.94 V and these waves disappeared and new waves appeared with time, owing to the lability in CH_3CN. On the reverse scan after the reductive scan to -1.4 V, the oxidation wave was observed at the same potential as the Ru(III)/Ru(II) couple for $[Ru^{III}Cl_2(NCCH_3)(bpca)]$. This result indicates that the reduction of $[Ru^{III}Cl_3(Hbpca)]$ afford $[Ru^{II}Cl_2(NCCH_3)(bpca)]^-$ in CH_3CN. At -40°C, the irreversible wave at -0.94 V changed into a reversible one as shown Fig. 6(a). The first reduction wave at -0.31 V disappeared by CPE at -0.6 V (see Fig. S7(b) in the Supplementary Information) and addition of equimolecular amounts of bases such as Bu_4NOH, LiOMe and NaOMe to the acetonitrile solution of $[Ru^{III}Cl_3(Hbpca)]$ as shown in Fig. 6(b), 6(c) and 6(d), respectively. The second reduction wave at -0.94 V was moved to the positive potential by addition of LiOMe and NaOMe as bases, while it was observed at the same potential using Bu_4NOH. The first wave at -0.31 V was assigned to the reduction of the proton contacted with the bpca ligand. In fact, during the CPE experiment at the potential of the reduction wave at -0.31 V (-0.6 V, see Fig. S7(b) in the Supplementary Information), the evolution of H_2 was observed by gas chromatography. Further reduction at -1.2 V revealed the formation of $[Ru^{II}Cl_2(NCCH_3)(bpca)]^-$ and $[Ru^{II}(NCCH_3)_3(bpca)]^+$ was confirmed by cyclic voltammetry (see Fig. S7(c) and (d) in the Supplementary Information). These results indicate that reduction and dissociation of the proton interacted to the bpca moiety occur and formation of $[Ru^{II}(NCCH_3)_3(bpca)]^+$ by CPE.

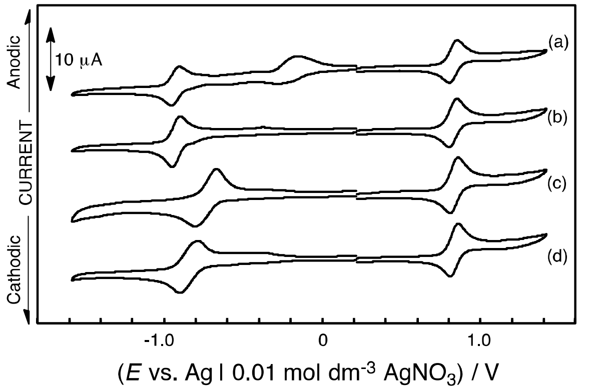


Fig. 6 Change of CV profile for $[Ru^{III}Cl_3(Hbpca)]$ by addition of bases in CH_3CN containing 0.10 mol dm^{-3} TEAP at -40°C; (a) $[Ru^{III}Cl_3(Hbpca)]$ (1.0 mmol dm^{-3}), (b) addition of Bu_4NOH, (c) addition of LiOMe, and (d) addition of NaOMe.

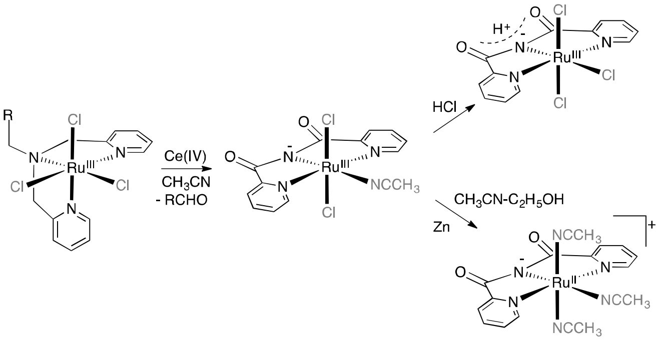
Formation of bis(2-pyridylcarbonyl)aminato moiety

The oxidation reactions of *fac*-$[Ru^{III}Cl_3(ebpma)]$ and *fac*-$[Ru^{III}Cl_3(bbpma)]$ were performed using equimolar amount of Ce(IV) in CH_3CN under air. The oxidation product of the tridentate bispyridylamine $[Ru^{III}Cl_2(NCCH_3)(bpca)]$ was isolated in good yields with the formation of aldehyde such as acetaldehyde and benzaldehyde that originated from the substituent groups bonded to the amine nitrogen of ebpma and bbpma. The oxidation process of *fac*-$[Ru^{III}Cl_3(ebpma)]$ was confirmed to be an one-electron process to afford a Ru(IV) form by electrochemical methods. To confirm the oxygen sources of bpca moiety, the ratio of oxygen to nitrogen after the reaction decreased in comparison with that of original atmosphere. The reaction under argon atmosphere was also performed to result in the formation of the same bpca complex with a byproduct which shows a strong NO stretching band in the IR spectrum and a characteristic reduction wave of the nitrosylruthenium moiety in the CV. Thus, the oxygen source of the carbonyl groups in the bpca ligand seems to come from dioxygen in air and/or nitrate ion of the oxidant.

Conclusions

The cooperative oxidation of the coordinated tridentate amine moiety occurred by the oxidation of the ruthenium centre from the +III state to the +IV state. The bpca ligand was formed via electron transfer between the ruthenium(IV) centre and the ebpma ligand to afford the ruthenium(III) complex containing the bpca ligand. The reactions of the present work are summarized in Scheme 1.

The bpca ligand and the related aminato ligands have been previously synthesized by hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine mediated with metal complexes[17-20] and organic syntheses or conversion of organic compounds on metal complexes.[23] Accumulation and magnetic properties of metal complexes bearing bpca have been reported in connection with magnetic interaction between metal centres.[17,18,25-27,29] This oxidation reaction of the coordinated amine ligand is highly unexpected and a first formation reaction of aminato ligand on the ruthenium centre. It is important for this reaction process that the ruthenium centre and the ebpma ligand cooperate through C-H activation of alkyl-arm and N-C activation of alkylamine moiety of the ebpma ligand.



Scheme 1 Reactions of the present work.

Notes and references

Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554 (Japan). Fax: 81 3 3238 3361; Tel: 81 3 3238 3478; E-mail: h-nagao@sophia.ac.jp

† Electronic Supplementary Information (ESI) available: Electrochemical properties, IR, NMR, and UV-vis spectra, and X-ray data. See DOI: 10.1039/b000000x/

1 V. Lyaskovskyy, B. Bruin, *ACS Catal.*, 2012, **2**, 270.

2 Special Issue on Coorporative & Redox Non-Innocent Ligands in Directiong Organometallic Reactivity: *Eur. J. Inorg. Chem.*, **2012**, 340.

3 K.-N. T. Tseng, A. M. Rizzi, N. K. Szymczak, *J. Am. Chem. Soc.*, 2013, **135**, 16352.

4 G. J. Christian, A. Llobet, F. Maseras, *Inorg. Chem.*, 2010, **49**, 5977.

5 C. Gemel, K. Folting, K. G. Caulton, *Inorg. Chem.*, 2000, **39**, 1593.

6 F. R. Keen, *Coord. Chem. Rev.*, 1999, **187**, 121.

7 E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang, D. Milstein, *J. Am. Chem. Soc.*, 2010, **132**, 8542.

8 F. Hasanayn, A. Baroudi, A. A. Bengali, A. S. Goldman, *Organometallics*, 2013, **32**, 6969.

9 C. A. Huff, Melanie S. Sanford, *ACS Catal*., 2013, **3**, 2412.

10 C. Gunanathan, D. Milstein, *Acc. Chem. Res.*, 2011, **44**, 588.

11 G. Zeng, S. Li, *Inorg. Chem.*, 2011, **50**, 10572.

12 H. Li, X. Wang, F. Huang, G. Lu, J. Jiang, Z.-X. Wang, *Organometallics*, 2011, **30**, 5233.

13 K. S. Sandhya, C. H. Suresh, *Organometallics*, 2011, **30**, 3888.

14 A. Friedrich, M. Drees, M. Käss, E. Herdtweck, S. Schneider, *Inorg. Chem.*, 2010, **49**, 5482.

15 S. Fukui, A. Kajihara, T. Hirano, F. Sato, N. Suzuki, H. Nagao, *Inorg. Chem.*, 2011, **50**, 4713.

16 S. Fukui, N. Suzuki, T. Wada, K. Tanaka, H. Nagao, *Organometallics*, 2010, **29**, 1534.

17 T. Kajiwara, H. Tanaka, M. Nakano, S. Takaishi, Y. Nakazawa, M. Yamashita, M., *Inorg. Chem.*, 2010, **49**, 8358.

18 H. Tanaka, T. Kajiwara, Y. Kaneko, S. Takaishi, M. Yamashita, *Polyhedron*, 2007, **26**, 2105.

19 X.-P. Zhou, D. Li, S.-L. Zheng, X. Zhang, T. Wu, *Inorg. Chem.*, 2006, **45**, 7119.

20 P. Paul, B. Tyagi, A. K. Bilakhiya, M. M.; Bhadbhade, E. Suresh, G. Ramachandraiah, *Inorg. Chem.*, 1998, **37**, 5733.

21 P. Paul, B. Tyagi, M. M. Bhadbhade, E. Suresh, *J. Chem. Soc, Dalton Trans.*, **1997**, 2273.

22 R. Sahu, S. K. Padhi, H. S. Jena, V. Manivannan, *Inorg. Chim. Acta*, 2010, **363**, 1448.

23 H. Chowdhury, S. H. Rahaman, R. Ghosh, S. K. Sarkar, H.-K. Fun, B. K. Ghosh, *J. Mol. Struct.*, 2007, **826**, 170.

24 J. M. Rowland, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.*, 2002, **41**, 2754.

25 A. M. Madalan, K. Bernot, F. Pointillart, M. Andruh, A. Caneschi, *Eur. J. Inorg. Chem.*, 2007, **35**, 5533.

26 M. Ferbinteanu, T. Kajiwara, K.-Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi, M. Yamashita, *J. Am. Chem. Soc.*, 2006, **128**, 9008.

27 T. Kajiwara, M. Nakano, Y. Kaneko, S. Takaishi, T. Ito, M. Yamashita, A. Igashira-Kamiyama, H. Nojiri, Y. Ono, N. Kojima, *J. Am. Chem. Soc.*, 2005, **127**, 10150.

28 B. Vangdal, J. Carranza, F. Lloret, M. Julve, J. Sletten, *J. Chem. Soc, Dalton Trans.*, **2002**, 566.

29 T. Kajiwara, R. Sensui, T. Noguchi, A. Kamiyama, T. Ito, *Inorg. Chim. Acta*, 2002, **337**, 299.

30 T. Kajiwara, T. Ito, *Angew. Chem. Int. Ed.*, 2000, **39**, 230.

31 A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, *Angew. Chem. Int. Ed.*, 2000, **39**, 3130.

32 S. Wocadlo, W. Massa, J.-V. Folgado, *Inorg. Chim. Acta*, 1993, **207**, 199.

33 S. Pal, M. K. Chan, W. H, Armstrong, *J. Am. Chem. Soc.*, 1992, **114**, 6398.

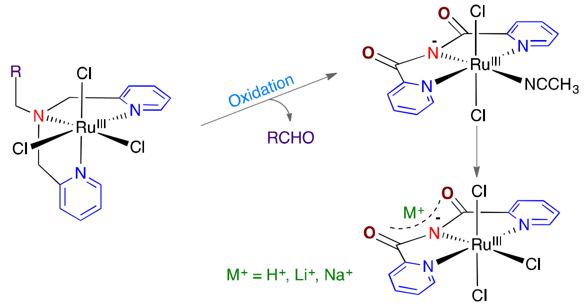
34 Y. Shimizu, S. Fukui, T. Oi, H. Nagao, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1285.

35 H.-Z. Xie, W.-J. Pan, W. Xu, J.-L. Lin, *Acta Cryst.*, 2008, **E64**, m1471.

36 H. Kooijman, S. Tanase, E. Bouwman, J. Reedijk, A. L. Spek, *Acta Cryst.*, 2006, **C62**, m510.

37 J. V. Folgado, E. Maetínez-Tamayo, A. Beltrán-Porter, D. Beltrán-Porter, Polyhedron, 1989, **8**, 1077.

Table of Contents Entry



Oxidation of the *facial*-type trichloridoruthenium(III) complex bearing ethylbis(2-pyridylmethyl)amine (ebpma), *fac*-[Ru^{III}Cl$_3$(ebpma)], with equimolecular amount of (NH$_4$)$_2$[Ce^{IV}(NO$_3$)$_6$] in acetonitrile afforded a ligand-base oxidation product of an acetonitriledichloridoruthenium(III) complex having bis(2-pyridylcarbonyl)aminato (bpca), [Ru^{III}Cl$_2$(NCCH$_3$)(bpca)]. The bpca moiety showed interaction with cations such as proton.