

Electrochemical studies of organometallic compounds

V*. Electrochemical reactions of ruthenium(II) isocyanide complexes

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Abstract

Electrochemical oxidations of *trans*-RuCl₂(RNC)₄ (**1**) and *trans,trans,trans*-RuCl₂(RNC)₂(PPh₃)₂ (**2**) (R = *t*-Bu, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂, 4-Br-2,6-Me₂C₆H₂, or 2,4-*t*-Bu₂-6-MeC₆H₂) are quasi-reversible. Half-wave potentials of **1**, which are higher than those of **2**, are increased by the electron-withdrawing ability of isocyanide ligands. Macroscopic electrolysis of **1** and **2** in a MeCN–NaClO₄ solution gives a reddish violet and a blue complex, [RuCl₂(RNC)₄](ClO₄) (**3**) and [RuCl₂(RNC)₂(PPh₃)₂](ClO₄) (**4**), respectively. An X-ray diffraction study of **3c** (R = 2,4,6-Me₃C₆H₂) shows that the stereochemistry of the starting compound **1c** is retained.

Introduction

Since ruthenium complexes can exist in various oxidation states, the chemistry is of interest in the context of redox behavior, catalytic activity, and material science such as an electrochromic behavior [1]. Carbonyl chemistry of ruthenium has been well documented, but there are a few reports on isocyanide complexes, which have an isoelectronic structure. Reduction of *trans*-RuCl₂(RNC)₄ (R = *t*-Bu or *i*-Pr) with sodium amalgam in the presence of excess isocyanide has been used to prepare Ru(*t*-BuNC)₅ and Ru₂(*i*-PrNC)₉ [2,3]. The cationic isocyanide species [Ru(MeNC)₆]²⁺ can be prepared by methylation of the hexacyanometallate anion

* For part IV see ref. 27.

with dimethyl sulfate, but other simple cations of this type have not been isolated [4]. Recently a convenient method for preparing homoleptic isocyanide complexes of the type $[\text{Ru}(\text{RNC})_6]^{2+}$ ($\text{R} = i\text{-Pr}$, $t\text{-Bu}$, or C_6H_{11}) was reported [5].

Electrochemical reactions are useful in preparing metal complexes. We have investigated the preparation and mechanism of the electrochemical reduction of $\text{MCl}_2(\text{RNC})_2$ ($\text{M} = \text{Pd}$ and Pt) into $\text{M}_2\text{Cl}_2(\text{RNC})_4$ and clusters ($\text{Pt}_3(\text{RNC})_6$ and $\text{HgPt}_6(\text{RNC})_{12}$) by electrochemical methods [6–9]. An extensive attempt to apply these methods to ruthenium(II) isocyanide complexes $\text{RuCl}_2(\text{RNC})_4$ was carried out, and presents new possibilities for electrochromic materials.

Recently the redox behavior of a series of $\text{RuCl}_2(\text{PR}_3)_2(\text{CO})_2$ and $\text{RuCl}_2(\text{PR}_3)_3(\text{CO})$ complexes has been studied by cyclic and differential-pulse voltammetry. The redox couple for the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ processes is electrochemically reversible [10].

Experimental

Apparatus. Infrared spectra were recorded on a JASCO A-100 spectrometer. ^1H NMR spectra were obtained on JEOL GX-400FT and Hitachi R-1100 spectrometers, with SiMe_4 as a reference. Electronic spectra were recorded on Hitachi Model 100-50 and JASCO U-best 100 instruments. Potentiostatic electrolyses under coulometry were carried out by use of a HUSO 956B potentiostat and a HUSO 321 potential scanning unit. Electrolytic cell was a conventional three-electrode system: a mercury pool electrode (ca. 12 cm^2) or Pt plate (ca. 12 cm^2) as a working electrode, a Pt wire as a counter electrode, and an $\text{Ag}/\text{AgNO}_3\text{-}[n\text{-Bu}_4\text{N}][\text{ClO}_4]/\text{MeCN}$ reference electrode, whose electrode potential was $328 \pm 3\text{ mV}$ versus a saturated calomel electrode (SCE). All potentials are relative to an aqueous SCE.

Materials. Acetonitrile was purified by distillation from calcium hydride. $[n\text{-Bu}_4\text{N}][\text{ClO}_4]$, the supporting electrolyte, was recrystallized from ethyl acetate before use. The isocyanides and $\text{RuCl}_2(\text{PPh}_3)_3$ were prepared by published procedures [11,12].

Some representative reactions are described.

Preparation of *trans*- $\text{RuCl}_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NC})_4$ (*1c*). A mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.50 g, 1.91 mmol) and mesityl isocyanide (1.10 g, 8.97 mmol) in ethanol (30 ml) was stirred in the presence of an excess of zinc amalgam at room temperature. After 2.5 h, the mixture was decanted and the solvent was removed in vacuo. The residue was chromatographed on alumina (containing 5% H_2O), using CH_2Cl_2 as an eluent. Removal of the solvent from the yellow solution and crystallization of the residue from CH_2Cl_2 and ether gave the yellow title compound (1.1 g, 53%).

IR(nujol): 2133 cm^{-1} ($\text{N}\equiv\text{C}$). Electronic spectrum (CH_2Cl_2): λ_{max} 265 (ϵ 5.01×10^4), 321 (2.31×10^4), and 379 (1.06×10^3) nm. ^1H NMR(CDCl_3): δ 2.29 (s, *p*-Me), 2.49 (s, *o*-Me) and 6.89 (s, *m*-H) ppm. Anal. Found: C, 63.70; H, 5.93; N, 7.60. $\text{C}_{40}\text{H}_{44}\text{N}_4\text{Cl}_2\text{Ru}$ calcd.: C, 63.82; H, 5.89; N, 7.44%.

The following complexes were prepared similarly:

***trans*- $\text{RuCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4 \cdot 1/2\text{CH}_2\text{Cl}_2$ (*1b*).** IR(nujol): 2135 cm^{-1} ($\text{N}\equiv\text{C}$). Electronic spectrum(CDCl_3): λ_{max} 262 (5.27×10^4), 323 (2.22×10^4), and 375 (1080) nm. ^1H NMR (CDCl_3): δ 2.55, 5.30 (CH_2) and ca. 7.15 (m, aromatic protons) ppm. Anal. Found: C, 59.83; H, 5.33; N, 7.43. $\text{C}_{36.5}\text{H}_{37}\text{N}_4\text{Cl}_3\text{Ru}$ calcd.: C, 59.93; H, 5.05; N, 7.58%.

trans-RuCl₂(4-Br-2,6-Me₂C₆H₂NC)₄ (1d, 58%). IR(nujol): 2120 cm⁻¹ (N≡C). Electronic spectrum (CH₂Cl₂): λ_{max} 270 (5.48 × 10⁴), 328 (2.56 × 10⁴), ca. 375 (sh) nm. Anal. Found: C, 42.81; H, 3.22, N, 5.62. C₃₉H₃₂N₄Br₄Cl₂Ru calcd.: C, 42.71, H, 3.19, N, 5.39%.

*trans-RuCl₂(2,4-*t*-Bu-2,6-MeC₆H₂NC)₄ (1e, 56%)*: IR(nujol): 2122 cm⁻¹ (N≡C). Electronic spectrum(CH₂Cl₂): λ_{max} 273 (63090), 327 (21600), and 378(sh) nm. Anal. Found: C, 70.77; H, 8.48; N, 5.39. C₆₄H₉₂N₄Cl₄ calcd.: C, 70.56; H, 8.82; N, 5.14%.

Preparation of trans,trans,trans-RuCl₂(2,4,6-Me₃C₆H₂NC)₂(PPh₃)₂ (2c). A mixture of RuCl₂(PPh₃)₃ (1.0 g, 1.04 mmol) and mesityl isocyanide (0.33 g, 2.28 mmol) was refluxed in CH₂Cl₂ (30 ml) for 2.5 h. The solvent was removed in vacuo and the orange solid was washed with ether to give yellow solids of **2c** containing 0.5 CH₂Cl₂ molecule (0.78 g, 76%). IR(nujol): 2100 cm⁻¹ (N≡C). ¹H NMR(CDCl₃): δ 1.99 (s, *o*-Me), 2.24 (s, *p*-Me) and ca. 6.5 (aromatic protons). Anal. Found: C, 66.31; H, 5.29; N, 2.81. C_{38.5}H₅₃N₂Cl₃P₂Ru calcd.: C, 66.03; H, 5.20; N, 2.72%. The analogous tert-butyl and 2,6-xylyl isocyanide complexes containing PPh₃ were also prepared. *trans,trans,trans-RuCl₂(*t*-BuNC)₂(PPh₃)₂ (2a, 68.3%)*. IR(nujol): 2130 cm⁻¹ (N≡C). ¹H NMR (CDCl₃): δ 1.00 and 7.2–8.2 (c, aromatic protons). *trans,trans,trans-RuCl₂(2,6-Me₂C₆H₃NC)₂(PPh₃)₂ (2b, 69.7%)*. IR(nujol): 2090 cm⁻¹ (N≡C). ¹H NMR(CD₂Cl₂): δ 3.00 (s, Me) and 7.2–8.2 (aromatic protons).

*Electrochemical oxidation of trans-RuCl₂(*t*-BuNC)₄ (1a)*. *trans-RuCl₂(*t*-BuNC)₄ (1a)* (0.27 g, 0.54 mmol) was dissolved in 0.1 mol dm⁻³ [n-Bu₄N][ClO₄]-MeCN (30 ml). The solution was deaerated by bubbling through with nitrogen. After the passage of 1.1 *F* of charge per mole of complex at 1.55 V (vs. SCE), the reddish violet solution was decanted and the solvent was removed in vacuo. The solid was extracted with CH₂Cl₂. Removal of the solvent and crystallization from CH₂Cl₂-ether gave reddish-violet crystals of *trans*-[RuCl₂(*t*-BuNC)₄](ClO₄) (**3a**) (0.17 g, 52%).

IR(nujol): 2182 cm⁻¹ (N≡C). ¹H NMR(CDCl₃): δ 10.36 (s, *t*-Bu). Anal. Found: C, 39.43; H, 5.92; N, 9.19. C₂₀H₃₆N₄Cl₃O₄Ru calcd.: C, 39.19; H, 5.92; N, 9.14%.

trans-[RuCl₂(2,6-Me₂C₆H₃NC)₄](ClO₄) · 0.5 H₂O (**3b**). IR(nujol): 2190 cm⁻¹ (N≡C). Anal. Found: C, 53.86; H, 4.61; N, 7.04. C₃₆H₃₇N₄O_{4.5}Cl₃Ru calcd.: C, 53.68; H, 4.63; N, 6.96%.

trans-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄) · H₂O (**3c**). IR(nujol): 2180 cm⁻¹ (N≡C). Anal. Found: C, 54.66; H, 5.24; N, 6.43. C₄₀H₄₆N₄O₅Cl₃Ru calcd.: C, 55.19; H, 5.33; N, 6.44%. ¹H NMR(CDCl₃): δ 5.82 and 13.87 (bs, *o*- and *p*-methyl).

trans,trans,trans-[RuCl₂(*t*-BuNC)₂(PPh₃)₂](ClO₄) (**4a, 67.9%**). IR(nujol): 2180 cm⁻¹ (N≡C). Electronic spectrum (CH₂Cl₂): λ_{max} 313 (2.60 × 10⁴). ¹H NMR(CDCl₃): δ ca. 9.00 (b, aromatic protons), 11.52 (bs, Me). Anal. Found: C, 57.26; H, 5.05; N, 3.02. C₄₆H₄₈N₂Cl₃O₄P₂Ru calcd.: C, 57.52; H, 5.04; N, 2.92%.

trans,trans,trans-[RuCl₂(2,6-Me₂C₆H₃NC)₂(PPh₃)₂](ClO₄) (**4b**). IR(nujol): 2170 cm⁻¹ (N≡C). Electronic spectrum (CH₂Cl₂): λ_{max} 314 (2.70 × 10⁴). Anal. Found: C, 60.68; H, 4.68; N, 2.69. C₅₄H₅₀N₂Cl₃O₅P₂Ru calcd.: C, 60.35; H, 4.68; N, 2.69%.

Chemical oxidation of trans-RuCl₂(2,6-Me₂C₆H₃NC)₄ with Ce(SO₄)₂. A mixture of *trans*-RuCl₂(2,4,6-Me₃C₆H₂NC)₄ (**1c**) (0.06 g, 0.08 mmol), Ce(SO₄)₂ (0.139 g, 0.42 mmol), and NH₄PF₆ (0.026 g, 0.16 mmol) in CH₂Cl₂ (15 ml) was stirred at room temperature. After 2 h, the violet mixture was filtered. Crystallization from

Table 1

Cyclic voltammetry of *trans*-RuCl₂(RNC)₄ (**1**) and *trans,trans,trans*-RuCl₂(PPh₃)₂(RNC)₂^a (**2**)

R		i_{pa}/i_{pc}	$E_{1/2}$ ^c (V)	ΔE ^b (V)
t-Bu	(1a)	1.11	1.02	0.09
		1.32	0.99 ^d	0.10
2,6-Me ₂ C ₆ H ₃	(1b)	1.27	1.26	0.09
		1.05	1.26 ^d	0.06
2,4,6-Me ₃ C ₆ H ₂	(1c)	1.39	1.20	0.08
4-Br-2,6-Me ₂ C ₆ H ₂	(1d)	–	1.35	0.10
2,4-t-Bu ₂ -6-MeC ₆ H ₂	(1e)	1.10	1.16	0.09
t-Bu	(2a)	1.15	0.79	0.08
2,6-Me ₂ C ₆ H ₃	(2b)	0.97	0.89	0.07
2,4,6-Me ₃ C ₆ H ₂	(2c)	1.07	0.85	0.08

^a Measured for sample in a ca. 1 mM solution of [n-Bu₄N][ClO₄]-MeCN (0.1 M) at a Pt working electrode, Ag/AgNO₃ reference electrode. Sweep rate: 0.10 V/s. ^b $\Delta E = |E_{pc} - E_{pa}|$ (vs. SCE). ^c $E_{1/2} = |E_{pc} + E_{pa}|/2$ (vs. SCE). ^d NaClO₄ as electrolyte.

CH₂Cl₂-ether gave violet crystals of *trans*-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄](PF₆)·(0.5)CH₂Cl₂ (**5c**) (0.0093 g, 12.4%). IR(nujol): 2270 and 2220 cm⁻¹ (N≡C). Anal. Found: C, 51.36; H, 4.87; N, 5.92. C_{40.5}H₄₅Cl₃F₆PRu calcd.: C, 51.74; H, 4.82; N, 5.96%.

Collection of X-ray diffraction data for *trans*-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄) (**3c**).

Blue crystals of *trans*-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄) (**3c**) suitable for an X-ray diffraction study were obtained from a mixture of CH₂Cl₂ and diethyl ether. A block-shaped crystal sealed in a glass tube capillary (0.7 mm) was used for the structure analysis. Diffraction data were collected at room temperature on a Rigaku RASA AFC-6 four-circle automated diffractometer. Preliminary measurements with this instrument showed the crystal to be triclinic in the space group *P*1 or *P* $\bar{1}$. Successful solution and refinement of the structure confirmed the latter to be the correct one. The unit cell dimensions were determined by a least-squares method with 20 reflections in the range 20° < 2θ < 30°. Three standard reflections were monitored before every 100 reflections and their intensities showed random variation within 2.0%. Intensities were corrected for Lorentz and polarization effects, and

Table 2

Cyclic voltammetry of *trans*-RuCl₂(2,4,6-Me₃C₆H₂NC)₄ (**3c**)^a

Solvent	Dielectric constant	$E_{1/2}$ ^b (V)	ΔE ^c (V)
Methylene chloride	8.93	0.70	0.11
acetonitrile	37.5	0.80	0.07
propylene	64.4	0.77	0.07
nitromethane	36.7	0.78	0.07

^a Sample in a ca. 1.0 mM solution in 0.1 M [n-Bu₄N][ClO₄]-solvent; sweep rate: 0.20 V/s. ^b $E_{1/2} = |E_{pc} + E_{pa}|/2$ (vs. ferrocene/ferrocenium). ^c $\Delta E = |E_{pc} - E_{pa}|$ (vs. ferrocene/ferrocenium).

Table 3

Selected bond lengths (Å) and angles (°) in [RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄) (**3c**)

Ru-Cl(1)	2.304(4)	Ru-Cl(2)	2.305(4)
Ru-C(1)	2.037(7)	Ru-C(2)	2.018(6)
Ru-C(3)	2.032(7)	Ru-C(4)	2.018(6)
C(1)-N(1)	1.138(9)	C(2)-N(2)	1.146(7)
C(3)-N(3)	1.134(9)	C(4)-N(4)	1.138(8)
Cl(1)-Ru-Cl(2)	178.47(7)	Cl(1)-Ru-C(1)	92.4(2)
Cl(1)-Ru-C(2)	86.7(2)	Cl(1)-Ru-C(3)	92.7(2)
Cl(1)-Ru-C(4)	90.0(2)	Cl(2)-Ru-C(1)	86.4(2)
Cl(2)-Ru-C(2)	92.4(2)	Cl(2)-Ru-C(3)	88.5(2)
Cl(2)-Ru-C(4)	90.9(2)	C(1)-Ru-C(2)	88.4(3)
C(1)-Ru-C(3)	174.7(3)	C(1)-Ru-C(4)	90.4(3)
C(2)-Ru-C(3)	90.3(3)	C(2)-Ru-C(4)	176.4(3)
C(3)-Ru-C(4)	91.2(3)	Ru-C(1)-N(1)	172.3(5)
Ru-C(2)-N(2)	174.0(5)	Ru-C(3)-N(3)	177.2(6)
Ru-C(4)-N(4)	177.3(6)	C(1)-N(1)-C(11)	170.7(6)
C(2)-N(2)-C(21)	172.4(6)	C(3)-N(3)-C(31)	177.3(7)
C(4)-N(4)-C(41)	174.4(8)		

an empirical absorption correction was made. The cyclic voltammetry data for **1**, **2** and **3c** are listed in Tables 1 and 2, selected bond lengths and angles in Table 3, and the crystallographic data are listed in Table 4.

Solution and refinement of the structure. The position of Ru atom was determined by a direct method by use of MULTAN78 [13]. The other atomic positions

Table 4

Crystallographic and experimental data for [RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄)

formula	RuCl ₃ O ₄ N ₄ C ₄₀ H ₄₄
molecular weight	852.2
crystal dimensions (mm)	0.80 × 0.50 × 0.25
crystal system	triclinic
space group	$P\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.794(11), 15.975(12), 8.084(10)
α , β , γ (°)	86.47(8), 104.29(8), 98.75(6)
<i>V</i> (Å ³)	2077(3)
<i>Z</i>	2
<i>d</i> (calcd) (g cm ⁻³)	1.363
radiation wavelength (Å)	0.7107 (Mo-K α)
scan method	$\omega(2\theta < 30^\circ)$, $\omega - 2\theta(30^\circ < 2\theta < 50^\circ)$
2 θ limit (°)	50
absorption correction (mm ⁻¹)	2.61
scan speed (deg min ⁻¹)	4
no. of data	6516
no. of data observed	5824 ($F_o > 3\sigma(F_o)$)
no. of variables	646
<i>R</i>	0.058
<i>R</i> _w	0.062 ($w = 1$)
data/variable	9.02

were subsequently found from a series of difference Fourier maps. Hydrogen atoms were placed at calculated positions ($C-H = 1.09 \text{ \AA}$ for methyl groups and 1.08 \AA for phenyl H atoms). Refinements were carried out with anisotropic thermal parameters for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms by block-diagonal least-squares techniques minimizing $\sum w(F_o - |F_c|)^2$. The refinement converged to $R = \sum |F_o - |F_c|| / \sum F_o = 0.058$, and $R_w = [\sum w(F_o - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.062$ ($w = 1$). The final difference Fourier synthesis revealed no unusual features; the highest peak was 0.97 e\AA^{-3} around the Ru atom. All calculations were performed by a FACOM M-780 at the Institute of Physical and Chemical Research with the universal program UNICS III [14]. Atomic scattering factors were taken from ref 15, and both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in F_c for all non-hydrogen atoms [16].

Results and discussion

Preparation of trans-RuCl₂(RNC)₄ and trans,trans,trans-RuCl₂(RNC)₂(PPh₃)₂.

The complex, *trans*-RuCl₂(RNC)₄ (**1a**: R = *t*-Bu; **1b**: R = 2,6-Me₂C₆H₃; **1c**: R = 2,4,6-Me₃C₆H₂; **1d**: R = 4-Br-2,6-Me₂C₆H₂; **1e**: R = 2,4-*t*-Bu₂-6-MeC₆H₂), was prepared by a published procedure by reduction of RuCl₃ · 3H₂O with zinc amalgam in the presence of isocyanide in ethanol [2]. Bulky 2,4,6-tri-*tert*-butylphenyl isocyanide complex was not obtained, because of the steric hindrance. The phosphine complex *trans,trans,trans*-RuCl₂(RNC)₂(PPh₃)₂ (**2a**: R = *t*-Bu, **2b**: R = 2,6-Me₂C₆H₃, **2c**: R = 2,4,6-Me₃C₆H₂) was obtained by the reaction of RuCl₂(PPh₃)₃ with the appropriate isocyanide.

Electrochemical reactions. Cyclic voltammograms of **1** and **2** in 0.1 mol dm^{-3} [*n*-Bu₄N][ClO₄]-MeCN solution were measured at a platinum electrode (Fig. 1). The peak current ratio, (i_{pc}/i_{pa}) remained close to unity for sweep rates, v from 0.2

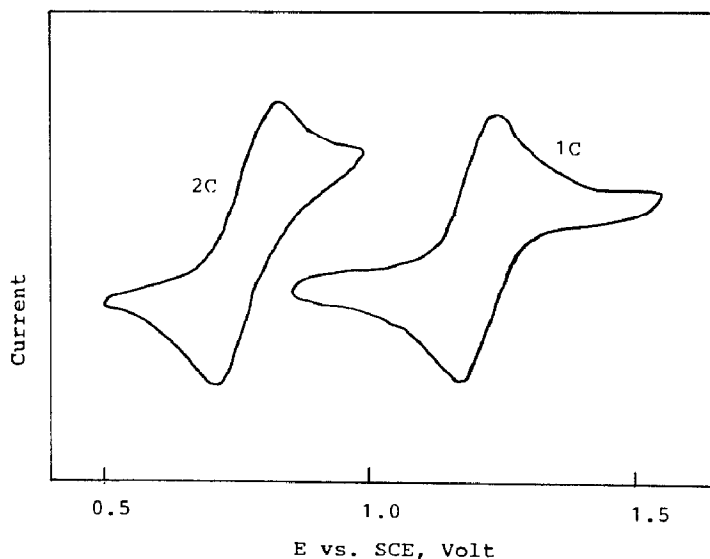


Fig. 1. Cyclic voltammetry of *trans*-RuCl₂(2,4,6-Me₃C₆H₂NC)₄ (**1c**) and *trans,trans,trans*-RuCl₂(2,4,6-Me₃C₆H₂NC)₂(PPh₃)₂ (**2c**) in a [*n*-Bu₄N][ClO₄]-MeCN solution (1.0 mM solution of the complex; sweep rate 0.1 V/s)

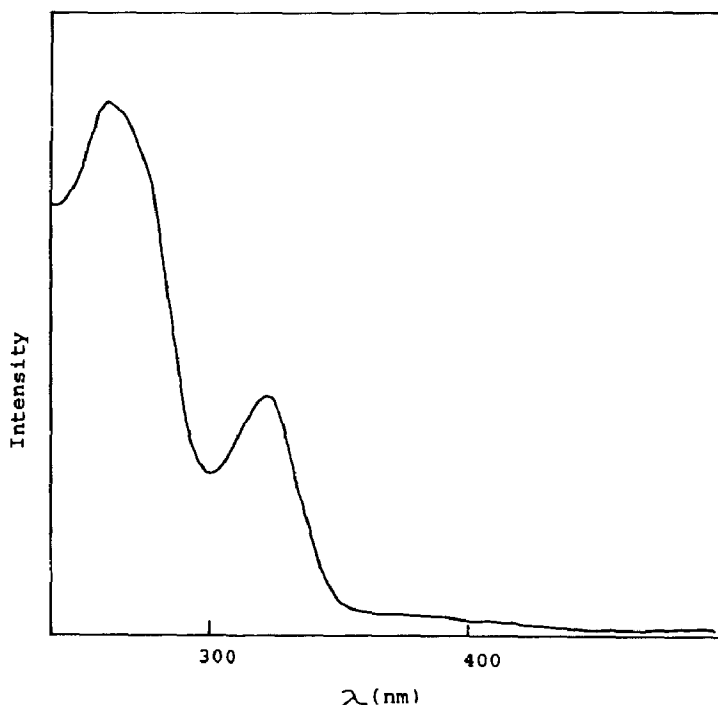


Fig. 2. Electronic spectrum of *trans*-RuCl₂(2,6-Me₂C₆H₃NC)₄ (**1b**) in CH₂Cl₂.

to 0.02 V/s and the $i_{pa}/v^{1/2}$ value was constant, and in accord with diffusion control. The potential separation between anodic and cathodic peak was almost constant at ca. 90 mV for a sweep rate of 0.1 V/s. The redox couple was assumed to be a quasi-reversible electron-transfer process or a process that approaches reversibility. The half-wave potentials, ($E_{1/2}$ vs. SCE) of RuCl₂(RNC)₄ (**1**) are comparable to those of RuCl₂(Ph_{*n*}Me_{3-*n*}P)₃(CO) and RuCl₂(Ph_{*n*}Me_{3-*n*}P)₂(CO)₂, whereas RuCl₂(RNC)₂(PPh₃)₂ was reduced at lower potential by ca. 0.21 V relative to those of the corresponding carbonyl complexes, RuCl₂(Ph_{*n*}Me_{3-*n*}P)₂(CO)₂ [10]. The $E_{1/2}$ values were found to depend the ligand and the solvent, but are independent of the electrolyte. Thus, $E_{1/2}$ of the phosphine complex (**2**) is lower than that of isocyanide complex (**1**). The $E_{1/2}$ value of isocyanide complexes decreases in the order **1d**, **1b**, **1c**, **1e**, **1a** for the complex (**1**) and **2b**, **2c**, **2a** for the complex (**2**). These are related with the π -acceptor ability. The $E_{1/2}$ value in a polar solvent is slightly lower than that in a nonpolar solvent, which indicates that the solvent molecule is involved in the ruthenium complex.

The electronic spectrum of **1b** is shown in Fig. 2. Similar spectra were observed for the other complexes.

Since these spectra are similar to those of Fe(CN)₂(RNC)₄, the band at 300 nm, which was previously assigned to a charge transfer (CT) in the iron complexes [17], is similarly assigned in the spectra of the ruthenium isocyanide complexes.

The relationship between the $E_{1/2}$ values and transition energies of CT band is shown in Fig. 3. An increase in the $E_{1/2}$ value results in a decrease in the CT band energy. This behavior of the CT band is probably attributable to a LMCT band. Similar trends have been observed in zerovalent chromium and molybdenum complexes such as Cr(RNC)_{6-*n*}(CO)_{*n*} and Mo(RNC)_{6-*n*}(CO)_{*n*} [18–20].

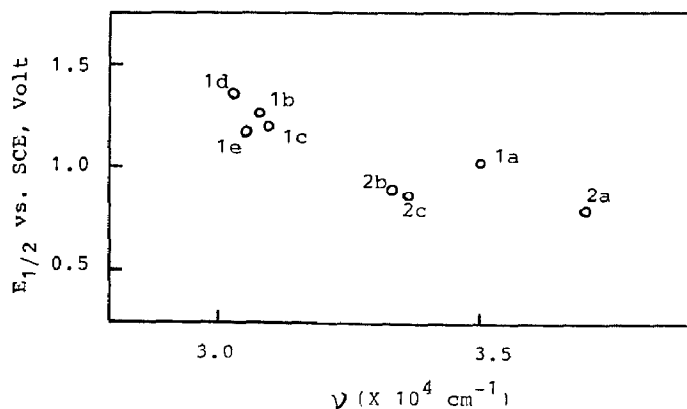


Fig. 3. Relation between the $E_{1/2}$ values and transition energies of CT band in *trans*- $\text{RuCl}_2(\text{RNC})_4$ (1) and *trans,trans,trans*- $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$ (2).

Coulometric studies

The electrolysis of (1a) at 1.1 V consumed 1 *F* (96.5 C) of charge per mole of complex. The color of the solution changed from yellow to reddish violet as charge was consumed. The spectra change is shown in Fig. 4. When this reddish violet solution was electrochemically reduced at 0.4 V, the mixture regenerated a yellow solution, showing electrochromic behavior. The oxidized product was isolated as reddish violet crystals, formulated as $[\text{RuCl}_2(\text{t-BuNC})_4](\text{ClO}_4)$ (3a). The infrared spectrum showed a characteristic band at 2220 cm^{-1} attributable to a N–C triple bond and a peak at 1090 cm^{-1} reminiscent of a ClO_4 group. The $\nu(\text{N}\equiv\text{C})$ band of the former is higher than that of the parent complex, which indicates that complex 3a is in a higher oxidation state than 2a. In the ^1H NMR spectrum the tert-butyl group showed a broad singlet (δ 10.36) in the lower magnetic field than the normal chemical shift, suggesting a paramagnetic compound. The spectroscopic data and the X-ray diffraction study of 3c (vide infra), indicate that this complex is in a *trans*-configuration. The stereochemistry of the Ru^{II} complex before and after the reaction remains unchanged. The ruthenium(III) complex *trans*- $[\text{RuCl}_2(\text{t-}$

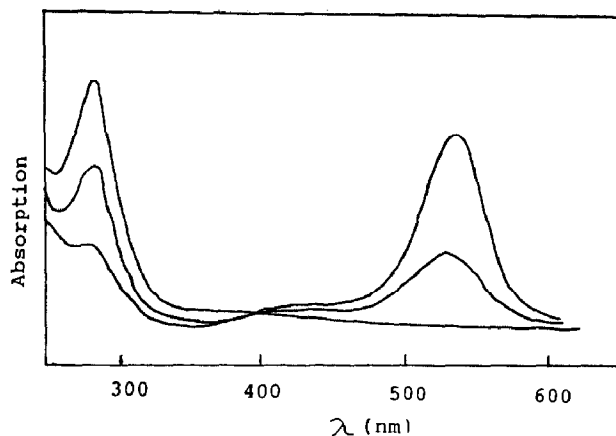


Fig. 4. Spectra change of *trans*- $\text{RuCl}_2(\text{t-BuNC})_4$ (1a).

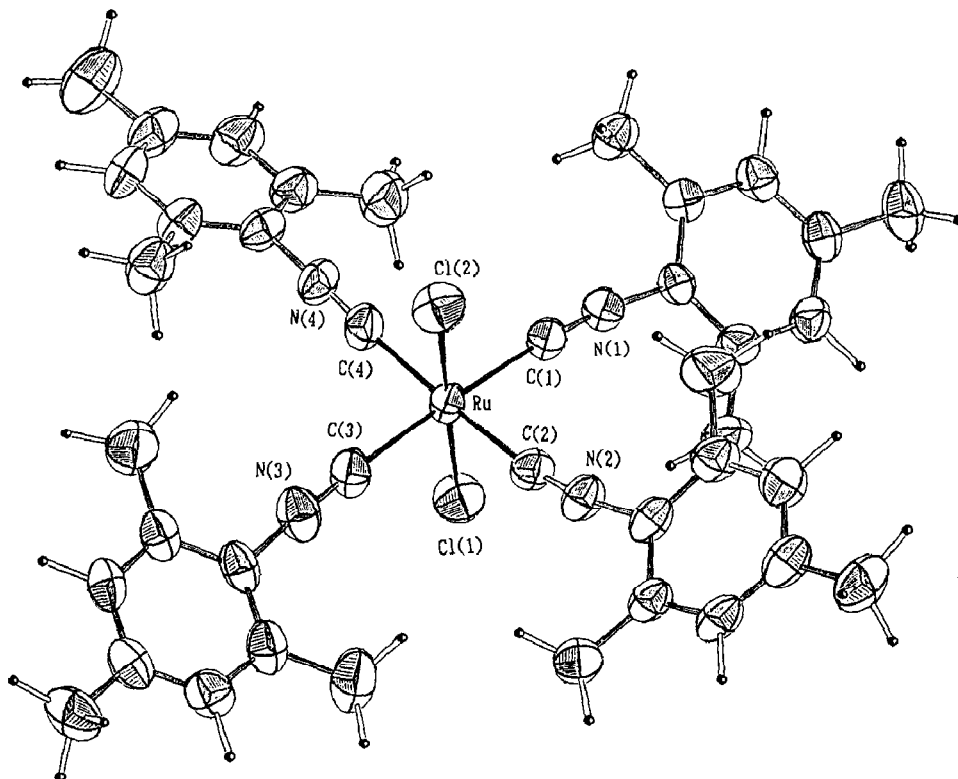


Fig. 5. Crystal structure of *trans*-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄][ClO₄] (3c).

BuNC)₄(PF₆) was also obtained from the chemical oxidation of **1c** with cerium(IV) sulfate in the presence of NH₄PF₆. A similar electrochemical oxidation of **1c** gives blue crystals formulated as [RuCl₂(2,4,6-Me₃C₆H₃NC)₄](ClO₄) · H₂O (**3c**). The Ru^{III} complexes having aromatic isocyanide ligands are generally less stable than those having tert-butyl isocyanide ligands. The ¹H NMR spectrum showed two broad singlets at δ 5.82 and 13.78 attributable to *o*- and/or *p*-methyl protons, and the signals from the aromatic protons were not assigned because of broadening of signals.

The one-electron oxidation of **2a** at 1.1 V gave a reddish violet solution, showing electrochromic behavior, from which reddish violet crystals were isolated, formulated as [RuCl₂(*t*-BuNC)₂(PPh₃)₂](ClO₄) (**4a**). The infrared spectrum showed only one peak, at 2180 cm⁻¹, attributable to the N–C triple bond, which indicates that the stereochemistry remains unchanged.

X-ray diffraction study of trans-[RuCl₂(2,4,6-Me₃C₆H₂NC)₄](ClO₄). The cationic molecule has an octahedral configuration, in which the Cl atoms are *trans* to one another (Fig. 5). The configuration is similar to that of the starting compound [1]. The C–Ru–C bond angles in the *cis* positions fall in the range 88.4° to 91.2° and the Cl–Ru–Cl bond angle is 178.5°. The average Ru–Cl bond length is 2.304 Å, which is shorter than those found in [RuCl(CO)(PhC=CHPh)(PPh₃)₂] (2.420(3) Å) [21] and [Ru₂Cl(Me₂PCH₂PMe₂)₂(PhNpy)₂][BPh₄] (2.480(5) Å) (PhNpy = 2-anilino-pyridine) [22], whereas the average Ru–C bond length of 2.026 Å is a little longer than those in [Ru₂(RNC)₁₀]²⁺ (R = 2,6-Me₂C₆H₃ [23] or PhCH₂ [24]) and

$[\text{Ru}_2(\text{CO})_2(\text{t-BuNC})_8]^{2+}$ [24]. The C–N bond length of 1.139 Å is normal. The bond angles of Ru–C–N and C–N–C fall in the range from 172° to 177°, and differ little from those found in many isocyanide complexes (Table 3). In the tetracoordinated $[\text{Rh}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4]^+(\text{TCNQ}^-)$ complex, a dihedral angle between the RhC_4 plane and one phenyl ring is tilted by ca. 70° and the other three phenyl groups are tilted below 25° [25]. In this complex the dihedral angles between the RhC_4 plane and four phenyl rings lie between 38° and 22°. Similar dihedral angles (average value: 36°) have been observed in hexacoordinated *trans*- $\text{FeCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4$ [26]. The large dihedral angles are probably responsible for the hexacoordination rather than the covalent radii of the central metal atoms.

Supplementary material available: Tables of positional thermal parameters, and tables of observed and calculated structure factor amplitudes are available from the authors.

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