

Reaction of a (Salen)ruthenium(VI) Nitrido Complex with Isocyanide

Hoi-Ki Kwong,[†] Wai-Lun Man,[†] Jing Xiang,[†] Wing-Tak Wong,[‡] and Tai-Chu Lau^{*,†}

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, China, and Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, China

Received December 7, 2008

The treatment of $[\text{Ru}^{\text{VI}}(\text{N})(\text{L})(\text{MeOH})]\text{PF}_6$ (**1**) ($\text{L} = N,N'$ -bis(salicylidene)-*o*-cyclohexyldiamine dianion) with 2 equiv of RNC ($\text{R} = (\text{a}) \text{ }^t\text{Bu}$, (b) Cy) in CH_2Cl_2 affords a mixture of blue *cis*- β - $[\text{Ru}^{\text{III}}(\text{NCNR})(\text{L})(\text{CNR})]$ (**2**) and green *trans*- $[\text{Ru}^{\text{III}}(\text{L})(\text{CNR})_2]\text{PF}_6$ (**3**) products. The reduction of **3** with a stoichiometric amount of Cp_2Co in CH_3CN gives red *trans*- $[\text{Ru}^{\text{II}}(\text{L})(\text{CNR})_2]$ (**4**). Refluxing **4** with 3 equiv of RNC in methanol in the presence of 5 equiv of NH_4PF_6 affords a yellow complex, *mer*- $[\text{Ru}^{\text{II}}(\eta^3\text{-HL})(\text{CNR})_3](\text{PF}_6)$ (**5**), in which the ligand is in an η^3 -coordination mode. These complexes are characterized by IR, UV–vis, ESI-MS, CV, magnetic measurements, and CHN elemental analysis. The structures of **2a**, **3a**, **4a**, **4b**, and **5a** have been determined by X-ray crystallography.

Introduction

Osmium(VI) nitrido complexes containing nitrogen-based ligands such as *cis*- or *trans*- $[\text{Os}^{\text{VI}}(\text{N})(\text{tpy})\text{Cl}_2]^+$ ($\text{tpy} = 2,2':6',2''$ -terpyridine), $[\text{Os}^{\text{VI}}(\text{N})(\text{tpm})\text{Cl}_2]^+$ ($\text{tpm} = \text{tris}(1\text{-pyrazolyl})\text{methane}$), $[\text{Os}^{\text{VI}}(\text{N})(\text{Tp})\text{Cl}_2]$ ($\text{Tp} = \text{hydrotris}(1\text{-pyrazolyl})\text{borate}$), and $[\text{Os}^{\text{VI}}(\text{N})(\text{bpy})\text{Cl}_3]$ ($\text{bpy} = 2,2'$ -bipyridine) have been shown to exhibit novel electrophilic properties. They react with a variety of nucleophiles such as phosphines,^{1–3} amines,^{4,5} azides,⁶ cyanide,⁷ alkenes,^{8–10} arylboranes and Grignard reagents,^{11,12} nitric oxide,¹³ amine

N-oxides,¹⁴ elemental sulfur and selenium,^{15,16} and thiols^{17,18} to produce the corresponding osmium species containing N–P, N–N, N–C, or N–E ($\text{E} = \text{O}, \text{S}, \text{Se}$) bonds.

We have been interested in exploring the new reactivity of nitrido complexes of osmium^{19–22} and ruthenium^{23,24} bearing salen or 8-quinolinato ligands. For example, we recently reported the synthesis and reactivity of a highly electrophilic, cationic (salen)ruthenium(VI) nitrido com-

* To whom correspondence should be addressed. E-mail: bhtclau@cityu.edu.hk.

[†] City University of Hong Kong.

[‡] University of Hong Kong.

- (1) Demadis, K. D.; Bakir, M.; Kleszczewski, B. G.; William, D. S.; Meyer, T. J.; White, P. S. *Inorg. Chim. Acta* **1998**, *270*, 511.
- (2) Bakir, M.; Dovletoglou, A.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835–2836.
- (3) Dehestani, A.; Kaminsky, W.; Mayer, J. M. *Inorg. Chem.* **2003**, *42*, 605–611.
- (4) Huynh, M. H. V.; El-Samanody, E. S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 1403–1404.
- (5) Huynh, M. H. V.; El-Samanody, E. S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 3075–3085.
- (6) Huynh, M. H. V.; Baker, R. T.; Jameson, D. L.; Labouriau, A.; Meyer, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 4580–4582.
- (7) Huynh, M. H. V.; White, P. S.; Carter, C. A.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3037–3039.
- (8) Brown, S. N. *J. Am. Chem. Soc.* **1999**, *121*, 9752–9753.
- (9) Brown, S. N. *Inorg. Chem.* **2000**, *39*, 378–381.
- (10) Maestri, A. G.; Cherry, K. S.; Toboni, J. J.; Brown, S. N. *J. Am. Chem. Soc.* **2001**, *123*, 7459–7460.
- (11) Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5595–5596.

- (12) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059–1071.
- (13) McCarthy, M. R.; Crevier, T. J.; Bennett, B.; Dehestani, A.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 12391–12392.
- (14) William, D. S.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 823–824.
- (15) Demadis, K. D.; El-Samanody, E. S.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 838–839.
- (16) Crevier, T. J.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 6607–6608.
- (17) Huynh, M. H. V.; White, P. S.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4101–4104.
- (18) Huynh, M. H. V.; Morris, D. E.; White, P. S.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2330–2333.
- (19) Wong, T. W.; Lau, T. C.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 6181–6186.
- (20) Chiu, S. M.; Wong, T. W.; Man, W. L.; Wong, W. T.; Peng, S. M.; Lau, T. C. *J. Am. Chem. Soc.* **2001**, *123*, 12720–12721.
- (21) Lai, S. W.; Lau, T. C.; Fung, W. K. M.; Zhu, N.; Che, C. M. *Organometallics* **2003**, *22*, 315–320.
- (22) Leung, C. F.; Wong, T. W.; Lau, T. C.; Wong, W. T. *Eur. J. Inorg. Chem.* **2005**, 773–778.
- (23) Man, W. L.; Tang, T. M.; Wong, T. W.; Lau, T. C.; Peng, S. M.; Wong, W. T. *J. Am. Chem. Soc.* **2004**, *126*, 478–479.
- (24) Man, W. L.; Lam, W. W. Y.; Yiu, S. M.; Lau, T. C.; Peng, S. M. *J. Am. Chem. Soc.* **2004**, *126*, 15336–15337.

plex.²³ This species undergoes direct nitrogen atom transfer to alkenes at room temperature to produce (salen)ruthenium aziridine complexes.²⁴

We report herein the reaction of a (salen)ruthenium(VI) nitrido complex, $[\text{Ru}^{\text{VI}}(\text{N})(\text{L})(\text{MeOH})](\text{PF}_6)$ (**1**; $\text{L} = N,N'$ -bis(salicylidene)-*o*-cyclohexyldiamine dianion) with isocyanides to produce carbodiimido and isocyanide complexes of ruthenium(III) and -(II).

Experimental Section

Materials. $[\text{Ru}^{\text{VI}}(\text{N})(\text{L})(\text{MeOH})](\text{PF}_6)$ (**1**) was prepared by a literature procedure.²³ The Schiff base ligand, H_2L ($\text{L} = N,N'$ -bis(salicylidene)-*o*-cyclohexylenediamine dianion) was synthesized by condensation of salicylaldehyde with *trans*-1,2-cyclohexyldiamine in refluxing ethanol. *tert*-Butyl isocyanide (tBuNC), cyclohexyl isocyanide (CyNC), and cobaltocene were purchased from Aldrich and used as received. Bu_4NPF_6 (Aldrich) was recrystallized three times from boiling ethanol and dried in vacuo at 120 °C for one day. Acetonitrile and dichloromethane used for electrochemistry were distilled over calcium hydride. All other chemicals were of reagent grade and used without further purification. All manipulations were performed without precaution to exclude air or moisture unless otherwise stated.

Physical Measurements. IR spectra were obtained as KBr discs using a Nicolet 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. The chemical shifts (δ) were reported with reference to tetramethylsilane (TMS). UV-vis spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer in 1 cm quartz cuvettes. Elemental analysis was performed using an Elementar Vario EL Analyzer. Magnetic measurements were performed at room temperature using a Sherwood magnetic balance (Mark II). Conductivity measurements were done with a Cole-Parmer 01481-61 conductivity meter. Electrospray ionization mass spectrometry (ESI-MS) was performed with a PE-SCIEX API 300 triple quadrupole mass spectrometer. Cyclic voltammetry was performed with a PAR model 273 potentiostat using a glassy carbon working electrode, a Ag/AgNO_3 (0.1 M in CH_3CN) reference electrode, and a Pt wire counterelectrode with ferrocene (FcP_2) as the internal standard.

Preparation. *cis*- β - $[\text{Ru}^{\text{III}}(\text{NCN}^i\text{Bu})(\text{L})(\text{CN}^i\text{Bu})]\cdot 3\text{H}_2\text{O}$ (**2a**) and *trans*- $[\text{Ru}^{\text{III}}(\text{L})(\text{CN}^i\text{Bu})_2]\text{PF}_6$ (**3a**). tBuNC (27 mg, 0.33 mmol) was added to an orange solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (50 mL), and the mixture was stirred for 24 h at room temperature. The green solution was evaporated to dryness; the residue was dissolved in a minimum amount of acetone and then loaded onto a silica gel column. The column was eluted with acetone to give a green band and then a blue band. Complex **2a** was obtained from the blue band after evaporation and recrystallization from acetone/*n*-pentane. Yield: (30%). Single crystals suitable for X-ray crystallography were obtained by the slow diffusion of *n*-pentane into an acetone solution of **2a**. IR (KBr, cm^{-1}): $\nu(\text{O}-\text{H})$ 3424; $\nu(\text{C}\equiv\text{N})$ 2156, 2103. Anal. calcd for $\text{C}_{30}\text{H}_{38}\text{N}_5\text{O}_2\text{Ru}\cdot 3\text{H}_2\text{O}$: C, 54.95; H, 6.76; N, 10.68. Found: C, 55.05; H, 6.51; N, 10.83. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 648 (6200), 526 (5100), 378 (8180), 337 (9500), 260 (57300). ESI-MS: m/z 603 ($[\text{M} + \text{H}]^+$). $\mu_{\text{eff}} = 2.07 \mu_{\text{B}}$. Complex **3a** was obtained from the green band after evaporation and recrystallization from acetone/ Et_2O . Yield: (30%). Single crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into an acetone solution of the compound. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2186; $\nu(\text{P}-\text{F})$ 845. Anal. calcd for $\text{C}_{30}\text{H}_{38}\text{N}_4\text{O}_2\text{PF}_6\text{Ru}$: C, 49.18; H, 5.23; N, 7.65. Found: C, 49.34;

H, 5.34; N, 7.86. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 739 (4170), 482 (1190), 328 (14700), 269 (59300), 237sh (45800), 216 (37700). ESI-MS: m/z 588 (M^+). $\mu_{\text{eff}} = 1.94 \mu_{\text{B}}$. Conductivity in CH_3CN : $\Lambda = 123 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

cis- β - $[\text{Ru}^{\text{III}}(\text{NCNCy})(\text{L})(\text{CNCy})]\cdot 3\text{H}_2\text{O}$ (**2b**) and *trans*- $[\text{Ru}^{\text{III}}(\text{L})(\text{CNCy})_2]\text{PF}_6$ (**3b**). These two solids were prepared by a procedure similar to that for **2a** and **3a** using cyclohexyl isocyanide. For **2b**, yield: (29%). IR (KBr, cm^{-1}): $\nu(\text{O}-\text{H})$ 3419; $\nu(\text{C}\equiv\text{N})$ 2163, 2102. Anal. calcd for $\text{C}_{34}\text{H}_{42}\text{N}_5\text{O}_2\text{Ru}\cdot 3\text{H}_2\text{O}$: C, 57.69; H, 6.83; N, 9.89. Found: C, 57.58; H, 6.72; N, 10.01. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 638 (3410), 525sh (2920), 377 (6520), 336 (7550), 230 (38900). ESI-MS: m/z 655 ($[\text{M} + \text{H}]^+$). $\mu_{\text{eff}} = 2.02 \mu_{\text{B}}$. For **3b**, yield: (30%). IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2194; $\nu(\text{P}-\text{F})$ 840. Anal. calcd for $\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_2\text{PF}_6\text{Ru}$: C, 52.04; H, 5.39; N, 7.14. Found: C, 51.85; H, 5.45; N, 7.20. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 748 (4280), 482 (1230), 329 (14200), 234sh (38300), 215 (36700). ESI-MS: m/z 640 (M^+). $\mu_{\text{eff}} = 1.98 \mu_{\text{B}}$. Conductivity in CH_3CN : $\Lambda = 125 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

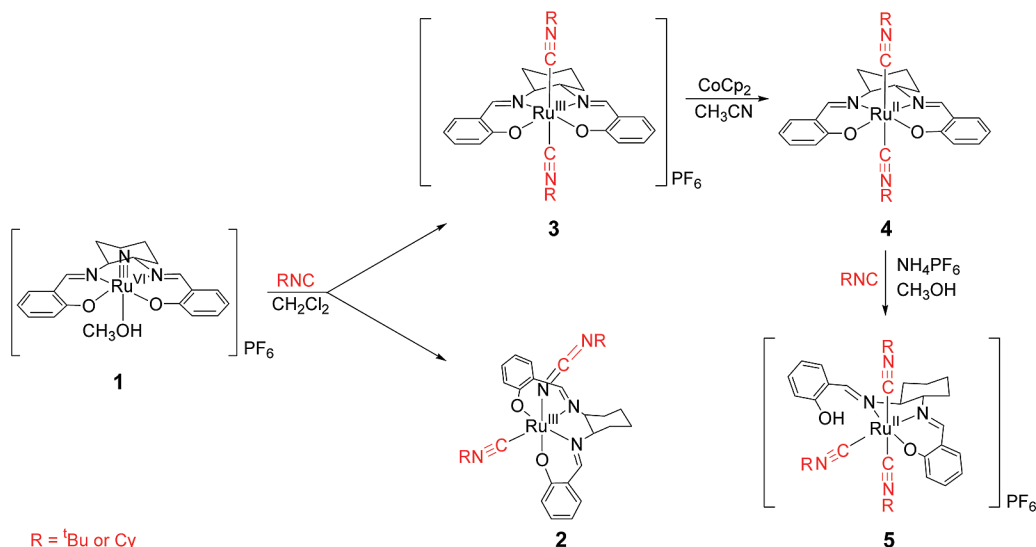
trans- $[\text{Ru}^{\text{II}}(\text{L})(\text{CN}^i\text{Bu})_2]$ (**4a**). Solid cobaltocene (27 mg, 0.14 mmol) was added to a green solution of **3a** (100 mg, 0.14 mmol) in acetonitrile (3 mL) under argon, and the solution was stirred for 30 min at room temperature. The resulting deep red solid was filtered, washed with acetonitrile, and then air-dried. Single crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into a CH_2Cl_2 solution of **4a**. Yield: (90%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.02 (s, 2H), 7.08–7.12 (t, 4H), 6.78–6.80 (d, 2H), 6.28–6.31 (t, 2H), 2.94–2.96 (d, 2H), 2.70–2.73 (d, 2H), 1.99–2.01 (d, 2H), 1.37–1.50 (m, 4H), 1.24 (s, 18H). IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2099. Anal. calcd for $\text{C}_{30}\text{H}_{38}\text{N}_4\text{O}_2\text{Ru}$: C, 61.31; H, 6.52; N, 9.53. Found: C, 61.09; H, 6.31; N, 9.49. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 451 (3110), 376 (13200), 336 (13700), 245sh (43800), 231 (50000). ESI-MS: m/z 588 (M^+).

trans- $[\text{Ru}^{\text{II}}(\text{L})(\text{CNCy})_2]$ (**4b**). This red solid was prepared by a procedure similar to that for **4a** using **3b**. Single crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into a CHCl_3 solution of **4b**. Yield: (88%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.02 (s, 2H), 7.07–7.10 (t, 4H), 6.78–6.80 (d, 2H), 6.33–6.36 (t, 2H), 3.80–3.82 (m, 2H), 2.99–3.02 (d, 2H), 2.71–2.74 (d, 2H), 1.99–2.01 (m, 4H), 1.18–1.64 (m, 22H). IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2108. Anal. calcd for $\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_2\text{Ru}$: C, 63.83; H, 6.62; N, 8.76. Found: C, 63.61; H, 6.63; N, 8.66. UV-vis (CH_3CN), λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 454 (2830), 377 (11900), 338 (12500), 246sh (38000), 230 (44300). ESI-MS: m/z 640 (M^+).

mer- $[\text{Ru}^{\text{II}}(\eta^3\text{-HL})(\text{CN}^i\text{Bu})_3]\text{PF}_6$ (**5a**). tBuNC (47 mg, 0.56 mmol) and NH_4PF_6 (140 mg, 0.86 mmol) were added to a solution of **4a** (110 mg, 0.17 mmol) in CH_3OH (10 mL), and the resulting solution was refluxed for 9 h under argon. The greenish yellow solution was filtered and evaporated to dryness, and the residue was redissolved in a minimum amount of CH_2Cl_2 and loaded onto a silica gel column. The column was first eluted with CH_2Cl_2 /acetone (20:1, v/v) to remove a trace amount of green species. The yellow band eluted with acetone was evaporated to dryness and then recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. Single crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into a CH_3CN solution of **5a**. Yield: (58%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.76 (s, 1H), 8.30 (s, 1H), 7.95–7.97 (d, 1H + s, 1H [OH]), 7.40–7.44 (t, 1H), 7.23–7.26 (d, 1H), 7.09–7.13 (t, 1H), 7.00–7.05 (m, 2H), 6.67–6.70 (d, 1H), 6.52–6.55 (t, 1H), 3.32–3.34 (m, 2H), 2.87–2.90 (d, 1H), 2.56–2.59 (d, 1H), 1.98–2.14 (m, 2H), 1.60–1.74 (m, 2H), 1.44 (s, 9H), 1.38–1.42 (m, 2H), 1.31 (s, 9H), 1.20 (s, 9H). IR (KBr, cm^{-1}): $\nu(\text{O}-\text{H})$ 3486; $\nu(\text{C}\equiv\text{N})$ 2191, 2147; $\nu(\text{P}-\text{F})$ 841. Anal. calcd for

Table 1. Crystal Data and Structure Refinement Details for Complexes **2a**·3H₂O, **3a**, **4a**, **4b**·CHCl₃, and **5a**·CH₃CN

	2a ·3H ₂ O	3a	4a	4b ·CHCl ₃	5a ·CH ₃ CN
formula	C ₃₀ H ₄₄ N ₅ O ₃ Ru	C ₃₀ H ₃₈ N ₄ O ₂ RuPF ₆	C ₃₀ H ₃₈ N ₄ O ₂ Ru	C ₃₅ H ₄₃ N ₄ O ₂ RuCl ₃	C ₃₇ H ₅₁ N ₆ O ₂ RuPF ₆
<i>M_r</i>	655.78	732.69	587.71	759.15	857.88
cryst dimensions/mm	0.41 × 0.25 × 0.05	0.18 × 0.21 × 0.46	0.04 × 0.05 × 0.45	0.24 × 0.23 × 0.08	0.20 × 0.42 × 0.45
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>Pbca</i> (No. 61)	<i>P21/c</i> (No. 14)	<i>C2/c</i> (No. 15)	<i>C2/c</i> (No. 15)	<i>P21/n</i> (No. 14)
<i>a</i> /Å	21.857(10)	15.966(2)	17.100(2)	34.738(5)	14.031(7)
<i>b</i> /Å	13.872(7)	14.595(2)	13.6041(18)	11.2485(16)	24.925(12)
<i>c</i> /Å	23.060(11)	14.252(2)	14.7986(19)	24.606(4)	14.199(7)
β	90	90	123.149(2)	132.242(1)	116.539(7)
<i>V</i> /Å ³	6992(6)	3320.9(8)	2882.4(6)	7118.0(18)	4442(4)
<i>Z</i>	8	4	4	8	4
ρ _{calcd} , mg m ⁻³	1.246	1.465	1.354	1.417	1.283
<i>F</i> (000)	2744	1500	1224	3136	1776
no. of reflns. collected	7932 (40866)	7721 (20184)	3299 (9730)	8116 (23684)	9793 (20363)
no. of obsd reflns. (<i>I</i> > 2σ(<i>I</i>))	3335 ^a	5769	2753	6392	6981
final <i>R</i> indices, <i>I</i> > 2σ(<i>I</i>) <i>R</i>	<i>R</i> = 0.0625, <i>wR</i> = 0.0706 ^a	<i>R</i> = 0.042, <i>wR</i> = 0.049	<i>R</i> = 0.0389, <i>wR</i> = 0.0751	<i>R</i> = 0.058, <i>wR</i> = 0.170	<i>R</i> = 0.079, <i>wR</i> = 0.326
GOF	1.094	1.087	1.015	1.046	1.308
no. of parameters	388	435	169	399	499

^a *I* > 1.5σ(*I*).**Scheme 1.** Synthesis of Compounds **2**–**5**

C₃₅H₄₈N₅O₂PF₆Ru: C, 51.47; H, 5.92; N, 8.57. Found: C, 51.63; H, 5.69; N, 8.72. UV–vis (CH₃CN), λ_{max} [nm] (ε [mol⁻¹ dm³ cm⁻¹]): 422sh (2610), 303 (12200), 236sh (34000), 215 (41500). ESI-MS: *m/z* 672 (M⁺).

mer-[Ru^{II}(η³-HL)(CNCy)₃]PF₆ (5b). This yellow solid was prepared by a similar procedure to that for **5a** using **4b** and cyclohexyl isocyanide. Yield: (60%). ¹H NMR (300 MHz, CD₂Cl₂): δ 8.75 (s, 1H), 8.28 (s, 1H), 7.66–7.68 (d, 1H), 7.37–7.41 (t, 1H), 7.21–7.23 (d, 1H), 7.10–7.12 (t, 1H + s, 1H [OH]), 7.01–7.08 (t, 2H) 6.64–6.66 (d, 1H), 6.47–6.51 (t, 1H), 3.89–3.94 (m, 2H), 3.36–3.39 (m, 3H), 2.88–2.91 (d, 1H), 2.56–2.59 (d, 1H), 2.02–2.14 (m, 2H), 1.83–1.95 (m, 2H), 1.28–1.69 (m, 32H). IR (KBr, cm⁻¹): ν(O–H) 3496; ν(C≡N) 2199, 2156; ν(P–F) 841. Anal. calcd for C₄₁H₅₄N₅O₂PF₆Ru: C, 55.03; H, 6.08; N, 7.83. Found: C, 54.85; H, 5.94; N, 7.92. UV–vis (CH₃CN), λ_{max} [nm] (ε [mol⁻¹ dm³ cm⁻¹]): 415sh (3040), 300 (12800), 236sh (36800), 218 (42700). ESI-MS: *m/z* 750 (M⁺).

X-Ray Crystallography. All measurements of **2a**·3H₂O, **3a**, **4a**, **4b**·CHCl₃, and **5a**·CH₃CN were made on either a Bruker Smart 1000 CCD or a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the ω-scan mode. Details of the intensity data collection and crystal data are given in Table 1. The data were corrected for Lorentz and polarization effects. Absorption corrections by the Ψ-scan method

or an approximation by interimage scaling were applied. The structures were resolved by direct methods²⁵ and expanded using Fourier techniques.²⁶ All calculations were performed using the Crystal Structure or TeXsan crystallographic software package from Molecular Structure Corporation.²⁷

Results and Discussion

The preparations of the various compounds described in this work are summarized in Scheme 1.

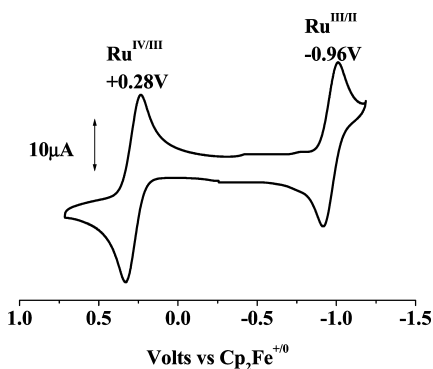
Addition of RNC (R = (a) ^tBu, (b) Cy) to [Ru^{VI}-(N)(L)(MeOH)]PF₆ (1). Treatment of **1** with 2 equiv of RNC in CH₂Cl₂ at ambient conditions results in a color change from orange to dark green after 1 day. *cis*-β-[Ru^{III}(NCNR)-

- (25) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
- (26) DIRDIF 99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Technical Report of the Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.
- (27) Single crystal structure analysis software: *CrystalStructure*, version 3.5.1; Rigaku/MS Corporation: The Woodlands, TX; Rigaku, Akishima: Tokyo, Japan, 2003. Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *Crystals*; Chemical Crystallography Lab: Oxford, U. K., 1996, issue 10.

Table 2. UV–Vis (CH₃CN), IR (KBr), and Electrochemical Data for Complexes **2**–**5**

complex	λ_{max} (nm (ϵ , M ^{−1} cm ^{−1}))	IR (KBr, cm ^{−1}) $\nu(\text{C}\equiv\text{N})$	$E_{1/2}$ (volts vs Cp ₂ Fe ⁺⁰) ^a	
			Ru ^{IV/III}	Ru ^{III/II}
2a	648 (6200), 526 (5100), 378 (8180), 337 (9500), 260 (57300)	2156, 2103	0.28 0.22 ^b	−0.96 −1.08 ^b
2b	638 (3410), 525sh (2920), 377 (6520), 336 (7550), 230 (38900)	2163, 2102	0.26 ^c 0.22 ^{b,c}	−0.94 −1.08 ^b
3a	739 (4170), 482 (1190), 328 (14700), 269 (59300), 237sh (45800), 216 (37700)	2186	0.87 ^c 0.90 ^{b,c}	−0.43 −0.47 ^b
3b	748 (4280), 482 (1230), 329 (14200), 234sh (38300), 215 (36700)	2194	0.89 ^c 0.85 ^{b,c}	−0.42 −0.47 ^b
4a	451 (3110), 376 (13200), 336 (13700), 245sh (43800), 231 (50000)	2099	0.92 ^{b,c}	−0.48 ^b
4b	454 (2830), 377 (11900), 338 (12500), 246sh (38000), 230 (44300)	2108	0.85 ^{b,c}	−0.46 ^b
5a	422sh (2610), 303 (12200), 236sh (34000), 215 (41500)	2191, 2147		0.43 ^c
5b	415sh (3040), 300 (12800), 236sh (36800), 218 (42700)	2199, 2156		0.45 ^c

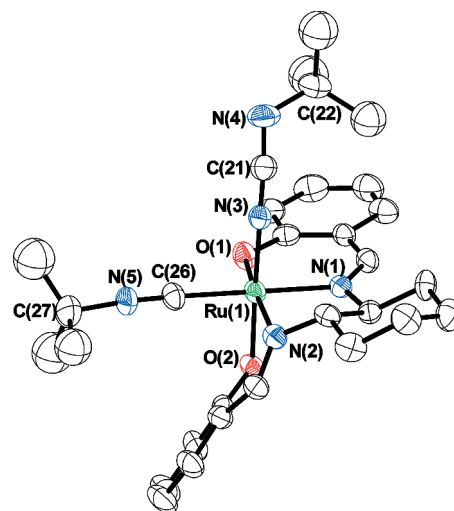
^a Glassy carbon working electrode, Pt counter electrode, Ag/AgNO₃ reference electrode, 0.1 M [NⁿBu₄]PF₆ in CH₃CN as supporting electrolyte. Ferrocene was added as an internal standard. The ΔE values for the reversible couples in CH₃CN are 65–75 mV at a scan rate of 100 mVs^{−1}. The ΔE values in CH₂Cl₂ are 90–100 mV at a scan rate of 100 mVs^{−1} and 68–74 mV at a scan rate of 20 mVs^{−1}. ^b In CH₂Cl₂. ^c Irreversible.

**Figure 1.** Cyclic voltammogram of **2a** in CH₃CN.

(L)(CNR)] (**2**) and *trans*-[Ru^{III}(L)(CNR)₂](PF₆) (**3**) have been isolated as blue and green solids, respectively (each in 30% yield), after chromatography.

Compounds **2a** and **2b** have room-temperature magnetic moments of $\mu_{\text{eff}} = 2.07$ and $2.02 \mu_{\text{B}}$ (solid sample, Gouy method), respectively, consistent with their formulation as Ru^{III} complexes with one unpaired electron. The cyclic voltammogram of **2a** in CH₃CN shows two reversible couples at +0.28 V and −0.96 V (vs Cp₂Fe⁺⁰), which are assigned to Ru^{IV/III} and Ru^{III/II} couples, respectively (Figure 1, Table 2). Similar electrochemical behavior is observed for other (salen)ruthenium(III) complexes.²⁸ The Ru^{IV/III} couple in **2b** is irreversible with $E_{\text{pc}} = +0.26$ versus Cp₂Fe⁺⁰. The IR spectrum (KBr) of **2a** shows two sharp bands at 2156 and 2103 cm^{−1}, which are assigned to $\nu(\text{C}\equiv\text{N})$ stretches of the RN≡C and RN=C=N[−] ligands, respectively. These bands occur at 2163 and 2102 cm^{−1} for **2b**. Carbodiimido complexes generally display a strong band at around 2100 cm^{−1}. For example, N=C=N stretches of carbodiimido complexes of zirconium²⁹ and palladium³⁰ occur at 2094 and 2140 cm^{−1}, respectively.

The molecular structure of **2a** has been determined by X-ray crystallography (Figure 2). The crystal data and

**Figure 2.** Molecular structure of **2a**·3H₂O. Thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

structural refinement details are given in Table 1. Selected bond distances and angles are listed in Table 3. The Ru atom adopts a distorted octahedral environment and is coordinated to one tetradentate salen, one ^tBuNCN, and one ^tBuNC ligand. The salen ligand is in a *cis*- β configuration with two N atoms and one O atom lying on the equatorial plane, while one O atom occupies an apical position. The *tert*-butylcarbodiimido unit has a typical diazacamulene structure (C(21)–N(3) = 1.194(14) Å, C(21)–N(4) = 1.240(15) Å, N(3)–C(21)–N(4) = 173.1(12)°).³¹ The Ru–N(3) bond distance is 1.980(7) Å, and the Ru–N(3)–C(21) angle (154.0(8)°) is acute. *cis*- β -Salen complexes of Ti,³² Cr,³³ Fe,³⁴ Co,³⁵ Mo,^{36,37} W,^{37,38} and Re³⁹ are known. [Ru(salen)(CO)₂] and [Ru(salen)(NO)(*cis*-stilbene sulfide)]⁺ have also been reported to have *cis* geometry, but these compounds have not been structurally characterized.^{40–42}

The formation of **2** is proposed to involve an initial nucleophilic addition of RNC to the nitrido ligand of **1** to give a [Ru^{IV}(NCNR)]⁺ intermediate, which presumably is then rapidly reduced by RNC.⁴³ [Ru^{IV}(NCNR)]⁺ is a reasonably strong oxidant (Table 2, $E_{1/2}$ of Ru^{IV/III} for **2a** = +0.28 V vs Cp₂Fe⁺⁰).

- (28) Man, W. L.; Kwong, H. K.; Lam, W. W. Y.; Xiang, J.; Wong, T. W.; Lam, W. H.; Wong, W. T.; Peng, S. M.; Lau, T. C. *Inorg. Chem.* **2008**, *47*, 5936–5944.
 (29) Kim, Y. J.; Lee, K. E.; Jeon, H. T.; Huh, H. S.; Lee, S. W. *Inorg. Chim. Acta* **2008**, *361*, 2159–2165.
 (30) Herrmann, H.; Fillol, J. L.; Wadepohl, H.; Gade, L. H. *Organometallics* **2008**, *27*, 172–174.

- (31) Gordon, M. S.; Fischer, H. *J. Am. Chem. Soc.* **1968**, *90*, 2471–2476.

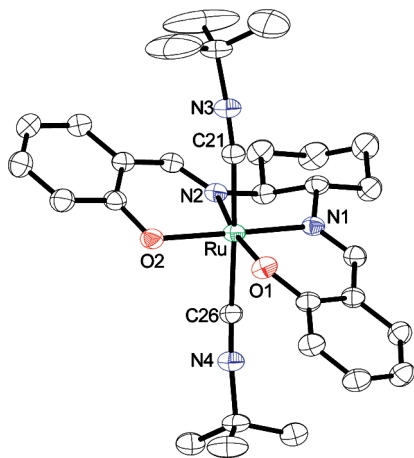


Figure 3. Molecular structure of the cation of **3a**. Thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

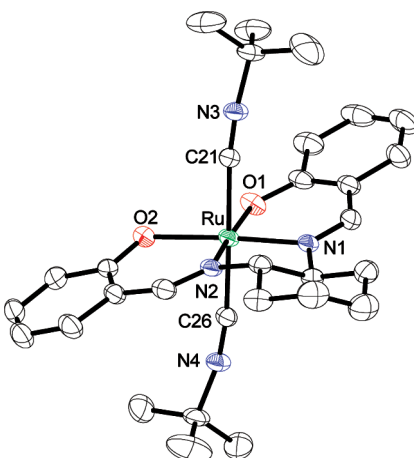


Figure 4. Molecular structure of **4a**. Thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of **2a**·3H₂O

Ru(1)–O(1)	2.010 (6)	Ru(1)–C(26)	1.979 (10)
Ru(1)–O(2)	2.017 (5)	N(3)–C(21)	1.194 (14)
Ru(1)–N(1)	2.050 (7)	N(4)–C(21)	1.240 (15)
Ru(1)–N(2)	2.014 (8)	N(5)–C(26)	1.155 (13)
Ru(1)–N(3)	1.980 (7)		
O(1)–Ru(1)–O(2)	87.9 (2)	N(1)–Ru(1)–N(2)	80.7 (3)
O(1)–Ru(1)–N(1)	93.1 (2)	N(1)–Ru(1)–N(3)	84.8 (3)
O(1)–Ru(1)–N(2)	169.8 (2)	N(1)–Ru(1)–C(26)	173.4 (3)
O(1)–Ru(1)–N(3)	91.0 (3)	N(2)–Ru(1)–N(3)	96.3 (3)
O(1)–Ru(1)–C(26)	92.9 (3)	N(2)–Ru(1)–C(26)	93.9 (3)
O(2)–Ru(1)–N(1)	93.6 (2)	N(3)–Ru(1)–C(26)	92.3 (3)
O(2)–Ru(1)–N(2)	84.5 (3)	Ru(1)–N(3)–C(21)	154.0 (8)
O(2)–Ru(1)–N(3)	178.0 (2)	Ru(1)–C(26)–N(5)	174.5 (9)
O(2)–Ru(1)–C(26)	89.4 (3)	N(3)–C(21)–N(4)	173.1 (12)

Early transition-metal or main-group carbodiimido complexes are generally prepared by the reaction of metal halides with trialkylstannyl (or trialkylsilyl) carbodiimides.⁴⁴ Carbodiimido complexes of Ni, Pd, and Pt have been prepared by the reaction of azido complexes with isocyanides.^{30,44} A zirconium carbodiimido complex has also been prepared from the corresponding (1-pyridinio)imido species.²⁹ Compounds **2a** and **2b** are the first examples of carbodiimido complexes of ruthenium; these complexes are also prepared by the unprecedented method of direct nucleophilic addition of isocyanide to a metal nitride (M≡N).

Synthesis and Characterization of *trans*-[Ru^{III}-(L)(CNR)₂]₂PF₆ (3**) and *trans*-[Ru^{II}(L)(CNR)₂] (**4**) (R = (a) **Bu**, (b) **Cy**).** Compound **2** does not react with excess RNC at room temperature over a period of 24 h, indicating that **3** is not formed from **2**. We have recently reported a general method for preparing (salen)ruthenium(III) complexes via ligand-induced N⋯N coupling of **1**.²⁸ Compound **3** is most likely formed from parallel N⋯N coupling in the reaction of **1** and RNC (eq 1).



Compounds **3a** and **3b** have $\mu_{\text{eff}} = 1.94$ and $1.98 \mu_{\text{B}}$, respectively (solid sample, Gouy method). Isocyanide complexes of Ru^{II} are common and well-documented,⁴³ however, there are few examples of ruthenium(III) isocyanide complexes.^{45–47} The IR spectrum (KBr) of **3a** shows a strong $\nu(\text{C}\equiv\text{N})$ stretch at 2186 cm^{-1} and an intense $\nu(\text{P}-\text{F})$ band at 845 cm^{-1} . The cyclic voltammogram of **3a** displays an irreversible Ru^{IV/III} wave at $E_{\text{pc}} = +0.87$ and a reversible Ru^{III/II} couple at $E_{1/2} = -0.43 \text{ V}$ versus $\text{Cp}_2\text{Fe}^{+/0}$ (Table 2). The ESI mass spectrum of **3a** (+ mode) in acetone displays a single peak at $m/z = 588$, which is assigned to the parent cation $[\text{Ru}(\text{L})(\text{CN}^{\text{tBu}})_2]^+$ (Figure S1, Supporting Information).

Compound **3** can be readily reduced to diamagnetic $[\text{Ru}^{\text{II}}(\text{L})(\text{CNR})_2]$ (**4**) with CoCp_2 or Zn/Hg . In the IR spectra, the $\nu(\text{C}\equiv\text{N})$ stretch is shifted from 2186 and 2194 cm^{-1} in **3a** and **3b** to 2099 and 2108 cm^{-1} in **4a** and **4b**, respectively. This shift to lower frequency is in accord with π -back-bonding between Ru(II) and RNC.

The structures of **3a**, **4a**, and **4b** have been determined by X-ray crystallography (Figure 3 and 4 and Figure S2,

- (32) Corden, J. P.; Errington, W.; Moore, P.; Wallbridge, M. G. H. *Chem. Commun.* **1999**, 323–324.
- (33) Lloret, F.; Julve, M.; Mollar, M.; Castro, I.; Lattore, J.; Faus, J.; Solans, X.; Morgenstern-Badarau, I. *J. Chem. Soc., Dalton. Trans.* **1989**, 729–738.
- (34) Lauffer, R. B.; Heistand, R. H.; Que, L. *Inorg. Chem.* **1983**, 22, 50–55.
- (35) Calligaris, M.; Manzini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton. Trans.* **1972**, 543–547.
- (36) Ramnauth, R.; Al-Juaid, S.; Motevalli, M.; Parkin, B. C.; Sullivan, A. C. *Inorg. Chem.* **2004**, 43, 4072–4079.
- (37) Motevalli, M.; Oduwale, A. D.; Parkin, B. C.; Ramnauth, R.; Sullivan, A. C.; Kaltsoyannis, N. *Dalton. Trans.* **2003**, 3591–3598.
- (38) Motevalli, M.; Parkin, B. C.; Ramnauth, R.; Sullivan, A. C. *J. Chem. Soc., Dalton. Trans.* **2000**, 2661–2662.
- (39) Ison, E. A.; Cessarich, J. E.; Travia, N. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, 129, 1167–1178.
- (40) Thornback, J. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 110–115.
- (41) Leung, W. H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1996**, 1229–1236.
- (42) Sauve, A. A.; Groves, J. T. *J. Am. Chem. Soc.* **2002**, 124, 4770–4778.
- (43) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Transition Metal*; John Wiley and Sons Ltd.: London, 1969.
- (44) Kim, Y. J.; Joo, Y. S.; Han, J. T.; Han, W. S.; Lee, S. W. *J. Chem. Soc., Dalton Trans.* **2002**, 3611–3618, and references therein.
- (45) al Dulaimi, J. P.; Clark, R. J. H.; Saavedra S., M.; Salam, M. A. *Inorg. Chim. Acta* **2000**, 300–302, 525–530.
- (46) Galardon, E.; Le Maux, P.; Paul, C.; Poriol, C.; Simonneaux, G. *J. Organomet. Chem.* **2001**, 629, 145–152.
- (47) Zavarine, I. S.; Kubiak, C. P.; Yamaguchi, T.; Ota, K.; Matsui, T.; Ito, T. *Inorg. Chem.* **2000**, 39, 2696–2698, and references therein.

Table 4. Selected Bond Distances (Å) and Angles (deg) of **3a** and **4a**

	3a	4a		3a	4a
Ru–O(1)	2.016 (2)	2.094 (1)	Ru–C(21)	2.031 (4)	2.008 (2)
Ru–O(2)	2.005 (3)	2.094 (1)	Ru–C(26)	2.046 (4)	2.008 (2)
Ru–N(1)	2.020 (3)	2.001 (1)	C(21)–N(3)	1.139 (5)	1.146 (3)
Ru–N(2)	2.019 (3)	2.001 (1)	C(26)–N(4)	1.146 (5)	1.146 (3)
O(1)–Ru–O(2)	98.7 (1)	91.76 (8)	N(1)–Ru–N(2)	81.9 (1)	83.35 (10)
O(1)–Ru–N(1)	90.0 (1)	92.47 (7)	N(1)–Ru–C(21)	94.0 (1)	93.90 (7)
O(1)–Ru–N(2)	171.0 (1)	175.43 (6)	N(1)–Ru–C(26)	89.2 (1)	87.73 (7)
O(1)–Ru–C(21)	93.3 (1)	94.43 (7)	N(2)–Ru–C(21)	83.5 (1)	87.73 (7)
O(1)–Ru–C(26)	85.3 (1)	84.06 (7)	N(2)–Ru–C(26)	98.3 (1)	93.90 (7)
O(2)–Ru–N(1)	170.7 (1)	175.43 (6)	N(3)–C(21)–Ru	170.7 (3)	171.1 (2)
O(2)–Ru–N(2)	89.7 (1)	92.47 (7)	N(4)–C(26)–Ru	170.0 (3)	171.1 (2)
O(2)–Ru–C(21)	88.8 (1)	94.43 (7)	C(21)–Ru–C(26)	176.5 (1)	177.8 (1)
O(2)–Ru–C(26)	88.2 (1)	84.06 (7)			

Supporting Information). The crystal data and structural refinement details are given in Table 1. Selected bond distances and angles are listed in Table 4. Compounds **3a** and **4a** are isostructural with distorted octahedral geometry; each Ru center is surrounded by a planar salen and two trans ^tBuNC ligands. The average Ru–C_{isocyanide} distances are 2.039 and 2.008 Å for **3a** and **4a**, respectively; the shorter Ru–C_{isocyanide} distance found in **4a** again demonstrates the presence of strong π -back-bonding between Ru(II) and RNC. The Ru–C_{isocyanide} distance of **4a** is comparable to that of [Ru^{II}(TPP)(CN^tBu)₂] (2.015(5) Å).⁴⁸ The Ru–C–N units are slightly bent (average $\angle$ Ru–C–N are 170.4° and 171.1° for **3a** and **4a** respectively). To our knowledge, the trinuclear complex, [Ru₃(μ_3 -O)(μ -CH₃CO₂)₆(X)₃] (X = xylyl isocya-

nide), is the only structurally characterized Ru^{III} isocyanide complex reported in the literature.⁴⁷

Synthesis and Characterization of an η^3 -Coordinated (Salen)ruthenium(II) Complex. As described above, the reaction of **1** with 2 equiv of RNC at room temperature produces **2** and **3**. No further reaction was observed when **3a** or **4a** was refluxed with excess ^tBuNC in methanol or ethanol for over 3 days under argon. However, by introducing 5 equiv of NH₄PF₆ as a proton source to **4a** and ^tBuNC in refluxing CH₃OH under argon, a color change from red to yellow was observed after 9 h. (No color change was observed when **3a** was used.) A yellow, air-stable crystalline compound (**5a**) was produced after workup, which is assigned as *mer*-[Ru^{II}(η^3 -HL)(CN^tBu)₃]PF₆. Compound **5b** was prepared similarly using **4b**. The formation of **5** is likely initiated by protonation of a phenoxy O atom of the salen ligand by NH₄PF₆, which would facilitate substitution by RNC. The IR (KBr) spectrum of **5a** shows one strong and one medium band at 2147 and 2191 cm⁻¹, respectively, which are assigned to the ν (C $\equiv$ N) stretches of ^tBuNC. There is a broad ν (O–H) peak at 3486 cm⁻¹ and an intense ν (P–F) band at 841 cm⁻¹ which are absent in **4a**. The ¹H NMR spectra of **5a** and **5b** in CD₂Cl₂ display well-resolved signals at normal field, indicating that these compounds are diamagnetic. Figure 5 shows the ¹H NMR spectrum of **5b** from 6–9 ppm. Unlike **4b**, the two imine protons occur as two distinct singlets at δ 8.75 and 8.28, indicating that they are in different environments. In the aromatic region (δ 6–8), there are in total nine protons, which are attributed to the eight aromatic protons on the ligand L plus one O–H proton (overlapped with one aromatic proton at ca. δ 7.1). Upon the addition of 5% D₂O (by volume), the integration of the resonance at δ 7.1 changes from two to one. For **5a**, the two imine protons again occur as two singlets at δ 8.76 and 8.30. The O–H proton overlaps with one aromatic proton at δ 7.95–7.97. The three ^tBuNC groups occur as three singlets at δ 1.44, 1.31, and 1.20. The ESI mass spectrum (+ mode) of **5a** in acetone displays a predominant peak at m/z = 672, which is assigned to the parent ion {[Ru(L)(CN^tBu)₃] $\cdot$ H}⁺ (Figure 6). This assignment is strongly

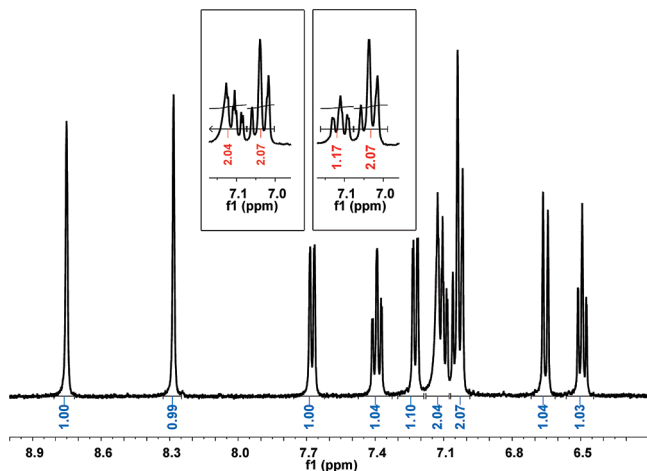


Figure 5. ¹H NMR spectrum of [Ru^{II}(HL)(CNCy)₃]PF₆ (**5b**) in CD₂Cl₂. Insets show the change of the peak at ca. δ 7.1 before (left) and after addition of 5% (v/v) D₂O (right).

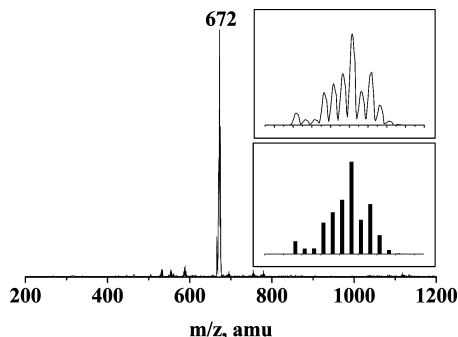


Figure 6. ESI mass spectrum (+ mode) of **5a** in acetone. Insets show the experimental (top) and calculated (bottom) isotopic patterns.

(48) Lee, F. W.; Choi, M. Y.; Cheung, K. K.; Che, C. M. *J. Organomet. Chem.* **2000**, 595, 114–125.

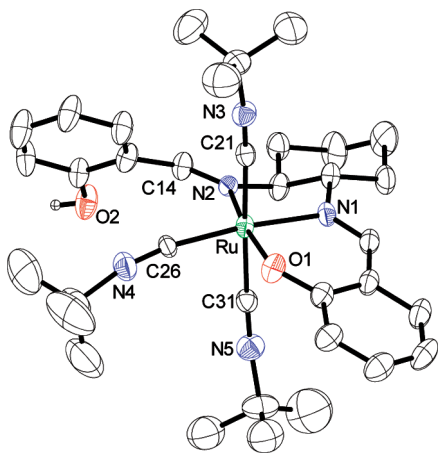


Figure 7. Molecular structure of cation of **5a**·CH₃CN. Thermal ellipsoids are drawn at 30% probability. H atoms (except O(2)–H) are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) of **5a**·CH₃CN

Ru–O(1)	2.093(10)	N(3)–C(21)	1.157(10)
Ru–N(1)	2.067(5)	N(4)–C(26)	1.152(8)
Ru–N(2)	2.084(11)	N(5)–C(31)	1.166(12)
Ru–C(21)	2.013(8)	N(1)–C(7)	1.288(9)
Ru–C(26)	1.959(5)	N(2)–C(14)	1.285(7)
Ru–C(31)	1.979(9)		
O(1)–Ru–N(1)	90.7(2)	N(2)–Ru–C(26)	99.4(2)
O(1)–Ru–N(2)	171.6(2)	N(2)–Ru–C(31)	92.1(2)
O(1)–Ru–C(21)	88.4(2)	C(21)–Ru–C(26)	94.6(2)
O(1)–Ru–C(26)	88.3(2)	C(21)–Ru–C(31)	174.1(3)
O(1)–Ru–C(31)	85.6(2)	C(26)–Ru–C(31)	85.4(2)
N(1)–Ru–N(2)	81.1(2)	Ru–N(1)–C(7)	124.0(4)
N(1)–Ru–C(21)	91.9(2)	Ru–N(2)–C(14)	131.8(4)
N(1)–Ru–C(26)	173.3(2)	Ru–C(21)–N(3)	177.1(6)
N(1)–Ru–C(31)	87.9(2)	Ru–C(26)–N(4)	169.6(4)
N(2)–Ru–C(21)	93.6(2)	Ru–C(31)–N(5)	171.1(7)

supported by the excellent agreement between the expanded and simulated isotopic patterns.

The molecular structure of **5a** is confirmed by X-ray crystallography; the cation is depicted in Figure 7. The crystal data and structural refinement details are given in Table 1. Selected bond distances and angles are listed in Table 5. The ruthenium atom is in a distorted octahedral environment with

three ^tBuNC ligands in the mer configuration. The salen ligand is only three-coordinated (two N atoms and one O atom) to ruthenium, with a dangling phenol group. To our knowledge, this is the first example of an η^3 -salen complex that has been structurally characterized. The Ru–N(1), Ru–N(2), and Ru–O(1) distances of 2.067(5), 2.084(11), and 2.093(10) Å, respectively, are similar to those in regular η^4 -(salen)ruthenium complexes. The equatorial Ru–C(isocyanide) distance (1.959(5) Å) is similar to that of the apical Ru–C distances (1.979(9) and 2.013(8) Å).

Summary

The electrophilic (salen)ruthenium(VI) nitrido complex [Ru^{VI}(N)(L)(MeOH)]⁺ reacts rapidly with isocyanide at room temperature to produce a mixture of *cis*- β -[Ru^{III}(NCNR)(L)-(CNR)] and *trans*-[Ru^{III}(L)(CNR)₂]⁺. *cis*- β -[Ru^{III}(NCNR)-(L)(CNR)] is the first example of a carbodiimido complex of ruthenium, which is formed from an unprecedented pathway involving the nucleophilic addition of isocyanide to the nitrido ligand. The salen ligand in the carbodiimido complex has a *cis*- β geometry. *trans*-[Ru^{III}(L)(CNR)₂]⁺ is formed by a parallel ligand-induced N⋯N coupling reaction of the nitrido complex. This complex is readily reduced to *trans*-[Ru^{II}(L)(CNR)₂], which further reacts with excess RNC in the presence of NH₄PF₆ to give *mer*-[Ru^{II}(η^3 -HL)(CNR)₃]PF₆, in which the salen is in an unprecedented η^3 -coordination mode.

Acknowledgment. The work described in this paper was supported by the Research Grants Council of Hong Kong (CityU 101505, CityU 2/06C).

Supporting Information Available: Crystallographic information files for **2a**·3H₂O, **3a**, **4a**, **4b**·CHCl₃, and **5a**·CH₃CN. ESI-MS of **3a** and molecular structure of **4b**·CHCl₃. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

IC802338F