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N–O bond cleavage and various bonding modes of the nitrato ligand in rhodium complexes: syntheses and structures of $[Cp^*Rh(\eta^1\text{-}NO_3)(\mu\text{-}Cl)]_2$, $\{[Cp^*RhCl(PPh_3)(CN{-}C_6H_{11})]_2(NO_2)(NO_3)\}\cdot 2H_2O$, $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^1,\mu\text{-}N_3)]_2$, $[Cp^*Rh(\eta^2\text{-}NO_3)(O_3SCF_3)]$, *trans*-$\{[Rh(PPh_3)_2(CN{-}2,6\text{-}Me_2C_6H_3)_2](NO_3)\}\cdot H_2O$, and $\{[Cp^*_2Rh_2(\eta^2,\mu\text{-}NO_2\text{-}N,O)_2(\eta^1,\mu\text{-}N_3)](PF_6)\}\cdot 0.5H_2O$

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Abstract

The addition of 2 equiv. of $AgNO_3$ to a dinuclear chloro-bridged Rh(III) compound, $[Cp^*RhCl_2]_2$, resulted in the replacement of the terminal chloro ligand to give $[Cp^*Rh(\eta^1\text{-}NO_3)(\mu\text{-}Cl)]_2$ (**1**). On the other hand, the reaction of $[Cp^*RhCl_2]_2$ with 4 equiv. of $AgNO_3$ led to the formation of a mononuclear bis(nitrato)-rhodium compound, $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)]$ (**2**). Compound **1** reacted with PPh_3 and cyclohexyl isocyanide ($CN{-}C_6H_{11}$) to give a chiral compound, $\{[Cp^*RhCl(PPh_3)(CN{-}C_6H_{11})]_2(NO_2)(NO_3)\}\cdot 2H_2O$ (**3**$\cdot 2H_2O$), which shows an unusual example of the nitrate-to-nitrite reduction in the rhodium coordination sphere. The reaction of compound **2** with either NaN_3 or N_3SiMe_3 gave a dinuclear (η^1-nitrato)-rhodium compound, $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^1,\mu\text{-}N_3)]_2$ (**4**). On the other hand, on addition of silver triflate (AgOTf), compound **2** underwent replacement to give a mononuclear (η^2-nitrato)-rhodium compound, $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ (**5**). In addition, compound **2** reacted with a mixture of PPh_3 and 2,6-dimethylphenyl isocyanide ($CN{-}2,6\text{-}Me_2C_6H_3$) to give *trans*-$\{[Rh(PPh_3)_2(CN{-}2,6\text{-}Me_2C_6H_3)_2](NO_3)\}\cdot H_2O$ (**6**$\cdot H_2O$), which exhibits the complete elimination of all ligands in compound **2** and indicates the formal reduction of the rhodium metal from +3 to +1. The nitro-rhodium compound, $\{[Cp^*_2Rh_2(\eta^2,\mu\text{-}NO_2\text{-}N,O)_2(\eta^1,\mu\text{-}N_3)](PF_6)\}\cdot 0.5H_2O$ (**7**$\cdot 0.5H_2O$), was prepared by the reaction of $[Cp^*RhCl(dppf)](PF_6)$ (dppf = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$) with a mixture of N_3SiMe_3 and $AgNO_3$, which also displays the N–O bond cleavage of nitrate (NO_3^-) to nitrite (NO_2^-). The structures of **1**, **3**$\cdot 2H_2O$, **4**, **5**, **6**$\cdot H_2O$, and **7**$\cdot 0.5H_2O$ were determined by X-ray diffraction.

Keywords: N–O bond cleavage; Rhodium; Nitrate-to-nitrite reduction

1. Introduction

Coordination chemistry of a nitrate anion (NO_3^-) has received considerable attraction because of interesting linkage isomerisms and various bonding modes in its compounds [1]. For example, Parkin and co-workers very recently reported that the coordination modes of the nitrato ligand correlate with the activities of metal-substituted carbonic anhydrases [2]. However, the reactivity of nitrato complexes has been relatively unexplored.

Chemical conversions of nitrogen oxides to nitrogen dioxide have long been investigated. These reactions proceed through the processes illustrated in Scheme 1: (1) the oxidation of nitrogen monoxide, (2) the reduction of nitrogen trioxide, (3) the disproportionation of nitrogen monoxide, and (4) the dissociation of dinitrogen tetraoxide [3–6]. Recently, Shapley and co-workers reported the synthesis of $Cp_2Rh_2(NO)(NO_2)$ from

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$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

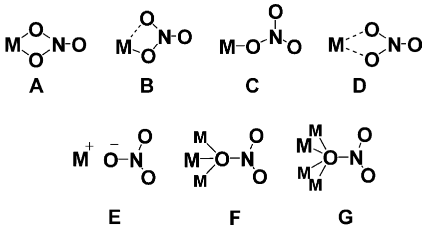
$$3NO \rightarrow N_2O + NO_2$$

$$N_2O_4 \rightarrow 2NO_2$$

Scheme 1.

$CpRh(CO)_2$ by a two-step reaction (NO bubbling and air oxidation). On the basis of ^1H NMR, IR, and mass spectra, they proposed the structure of this compound to contain a bridging NO and a *N*,*O*-bridging NO_2^- ligand [7].

Several bonding types of the nitrato ligand are now known [1]: symmetrical bidentate (**A**) [8], asymmetrical bidentate (**B**) [2,9], monodentate (**C**) [10], long-bonded symmetrical (**D**) [11], uncoordinate (**E**) [12], η^1,μ^3(**F**) [13], and η^1,μ^4(**G**) [14]. The addition of two-electron, neutral ligands converts **A**- and **C**-type compounds to the **C**- and **E**-type ones, respectively, through the modification of the hapticity of the nitrato ligand.



Because the Rh-nitrato compounds are somewhat rare and because their reactivity has been relatively unexplored, we set out to prepare this type of rhodium compounds and investigate their reactivity. Herein, we report the preparation and structures of rhodium-nitrato or -nitro complexes, together with some examples of their reactivity, including an unusual N–O bond cleavage of nitrato (NO_3^-) to nitro (NO_2^-).

2. Experimental

All reactions have been performed under argon at room temperature (r.t.). Rhodium(III) chloride hydrate, silver nitrate, silver trifluoromethanesulfonate, triphenylphosphine, 1,2,3,4,5-pentamethylcyclopentadiene (Cp*), sodium azide, trimethylsilyl azide, 2,6-dimethylphenyl isocyanide, and cyclohexyl isocyanide were purchased. $[Cp^*RhCl_2]_2$ [15] and $[Cp^*RhCl(dppf)](PF_6)$ (dppf = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$) [16] were prepared by the literature methods. All products were recrystallized from either dichloromethane–pentane or dichloromethane–hexane.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer. IR spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

2.1. $[Cp^*Rh(\eta^1\text{-}NO_3)(\mu\text{-}Cl)]_2$ (**1**)

$[Cp^*RhCl_2]_2$ (100 mg, 0.12 mmol) and $AgNO_3$ (41 mg, 0.24 mmol) in a mixed solvent (30 ml) of acetone and dichloromethane (1:1) were stirred for 3 h, and then the solvent was removed under vacuum. The resulting solids were extracted with dichloromethane (30 ml × 2), and then the solvent was removed. The solid product was washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried under vacuum (red crystals, 105 mg, 96.4%). M.p. = 211–213 °C (dec.). IR (KBr): 1458 (NO). 1382 (NO) cm^{-1}. ^1H NMR: δ 1.61 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 94.58 (d, $J_{Rh-C} = 7.4$ Hz, C_5Me_5), 9.11 (s, C_5Me_5). *Anal.* Calc. for $C_{20}H_{30}Cl_2N_2O_6Rh_2$: C, 35.79; H, 4.51; N, 4.17. Found: C, 35.56; H, 4.42; N, 4.13%.

2.2. $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)]$ (**2**)

This compound was prepared analogously to compound **1**. $[Cp^*RhCl_2]_2$ (100 mg, 0.12 mmol) was treated with $AgNO_3$ (82 mg, 0.48 mmol) to give orange crystals (109 mg, 93.1%). Compound **2** was identified by the comparison with literature data [17,18].

2.3. $\{[Cp^*RhCl(PPh_3)(CN\text{–}C_6H_{11})]_2(NO_2)(NO_3)\}\cdot 2H_2O$ (**3**$\cdot 2H_2O$)

Compound **1** (100 mg, 0.28 mmol) and PPh_3 (145 mg, 0.55 mmol) in dichloromethane (30 ml) were stirred for 3 h. Then, cyclohexyl isocyanide (68 µl, 0.55 mmol) in dichloromethane (15 ml) was added. The reaction mixture was further stirred for 3 h, and the solvent was removed. The resulting yellow solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (yellow crystals, 132 mg, 90.4%). M.p. = 159–161 °C. IR (KBr): 2205 (CN), 1437 (NO), 1382 (NO) cm^{-1}. ^1H NMR: δ 1.62 (s, C_5Me_5), 1.98–1.44 (10H, m, Cy), 4.04 (1H, br, *ipso*-H(Cy)), 7.69–7.47 (15H, m, Ph). $^{13}C\{^1H\}$ NMR: δ 105.50 (d, $J_{Rh-C} = 6.6$ Hz, C_5Me_5), 9.45 (s, C_5Me_5), 57.37–22.72 (m, Cy), 134.41–128.68 (m, Ph). $^{31}P\{^1H\}$ NMR: δ 35.23 (d, $J_{P-Rh} = 122$ Hz). *Anal.* Calc. for $C_{70}H_{84}Cl_2N_4O_7P_2Rh_2$: C, 58.71; H, 5.91; N, 3.91. Found: C, 58.74; H, 5.81; N, 3.85%.

2.4. $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^1,\mu\text{-}N_3)]_2$ (**4**)

2.4.1. Method A

A dichloromethane solution (30 ml) containing compound **2** (100 mg, 0.28 mmol) and NaN_3 (54 mg, 0.83 mmol) was stirred for 24 h and filtered, and the solvent was removed. The resulting solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (orange–red crystals, 84 mg, 89.2%).

2.4.2. Method B

A dichloromethane solution (30 ml) containing compound **2** (100 mg, 0.28 mmol) and N_3SiMe_3 (109 μl, 0.83 mmol) was stirred for 24 h, and the solvent was removed. The resulting solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (80 mg, 84.7%). M.p.: 219–221 °C. IR (KBr): 2058 (N_3), 1464 (NO), 1382 (NO) cm^{-1}. ^1H NMR: δ 1.61 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 94.14 (d, $J_{Rh-C} = 9.3$ Hz, C_5Me_5), 8.75 (s, C_5Me_5). *Anal.* Calc. for $C_{20}H_{30}N_8O_6Rh_2$: C, 35.10; H, 4.42; N, 16.38. Found: C, 35.49; H, 4.50; N, 16.49%.

2.5. $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ (**5**)

Compound **1** (100 mg, 0.28 mmol) and AgOTf (71 mg, 0.28 mmol) in a mixed solvent (30 ml) of acetone and dichloromethane (1:1) were stirred for 3 h, and then the solvent was removed. The remaining solids were extracted with dichloromethane (30 ml × 2), and the solvent was removed. The resulting solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (orange crystals, 105 mg, 84.7%). M.p. = 173–175 °C. IR (KBr): 1471 (NO), 1384 (NO) cm^{-1}. ^1H NMR: δ 1.80 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 93.99 (d, $J_{Rh-C} = 10.1$ Hz, C_5Me_5), 9.33 (s, C_5Me_5). *Anal.* Calc. for $C_{11}H_{15}F_3NO_6SRh$: C, 29.41; H, 3.37; N, 3.12; S, 7.14. Found: C, 28.96; H, 3.50; N, 3.09; S, 7.19%.

2.6. *trans*-$\{[Rh(PPh_3)_2(CN\text{–}2,6\text{-}Me_2C_6H_3)_2](NO_3)\}\cdot H_2O$ (**6**$\cdot H_2O$)

Compound **1** (100 mg, 0.28 mmol) and PPh_3 (145 mg, 0.55 mmol) in dichloromethane (30 ml) were stirred for 3 h. 2,6-Dimethylphenyl isocyanide (72 mg, 0.55 mmol) in dichloromethane (15 ml) was then slowly added. The reaction mixture was further stirred for 3 h, and the solvent was removed. The resulting solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (yellow crystals, 114 mg, 42.6%). M.p. = 157–159 °C. IR (KBr): 2122 (CN), 1434 (NO), 1384 (NO) cm^{-1}. ^1H NMR: δ 1.64 (s, $Me_2C_6H_3$), 1.62 (s, $Me_2C_6H_3$), 7.03–6.84 (m, $Me_2C_6H_3$), 7.67–7.33 (30H, m, Ph). $^{13}C\{^1H\}$ NMR: δ 134.86–128.35 (m, $Me_2C_6H_3$ and Ph), 18.59 (s, $Me_2C_6H_3$). $^{31}P\{^1H\}$ NMR: δ 31.55 (d, $J_{P-Rh} = 122$ Hz). *Anal.* Calc. for $C_{54}H_{50}N_3O_4P_2Rh$: C, 66.87; H, 5.20; N, 4.33. Found: C, 66.99; H, 5.28; N, 4.29%.

2.7. $\{[Cp^*_2Rh_2(\eta^2,\mu\text{-}NO_2\text{-}N,O)_2(\eta^1,\mu\text{-}N_3)](PF_6)\}\cdot 0.5H_2O$ (**7**$\cdot 0.5H_2O$)

$[Cp^*RhCl(dppf)](PF_6)$ (100 mg, 0.12 mmol) and N_3SiMe_3 (16 μl, 0.12 mmol) in a mixed solvent (30 ml) of acetone and dichloromethane (1:1) were stirred for 24 h, and then $AgNO_3$ (62 mg, 0.36 mmol) was added. The reaction mixture was stirred for 12 h, and the solvent was removed. The remaining solids were extracted with dichloromethane (30 ml × 2), and the solvent was removed again. The resulting solids were washed with hexane (20 ml) and diethyl ether (20 ml × 2), and then dried (orange crystals, 11 mg, 25.9%). M.p. = 221–223 °C. IR (KBr): 2057 (N_3), 1459 (NO), 1378 (NO), 838 (PF) cm^{-1}. ^1H NMR: δ 1.72, 1.65, 1.63, 1.53 (all s, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 98.79 (d, $J_{Rh-C} = 8.8$ Hz, C_5Me_5), 8.96 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR: δ −144.22 (sep, $J_{P-F} = 695.9$ Hz, PF_6). *Anal.* Calc. for $C_{20}H_{31}F_6N_5O_{4.5}PRh_2$: C, 31.43; H, 4.09; N, 9.17. Found: C, 30.98; H, 4.15; N, 9.07%.

2.8. X-ray structure determination

All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by the least-squares analyses of the setting angles of 23 (for **1**), 24 (for **3**$\cdot 2H_2O$), 29 (for **4**), 28 (for **5**), 23 (for **6**$\cdot H_2O$) and 26 (for **7**$\cdot 0.5H_2O$) reflections in the range of $15.0 < 2\theta < 25.0°$. Three check-reflections were measured every 100 reflections throughout data collection. Intensity data were corrected for Lp. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of SHELXTL programs [19].

All crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically except the fluorine atoms in compound **7**$\cdot 0.5H_2O$, in which the counter-anion (PF_6^-) exhibited an extreme structural disorder and, therefore, the fluorine atoms were refined isotropically. All hydrogen atoms were generated in ideal positions and refined in a riding model.

3. Results and discussion

3.1. Preparation

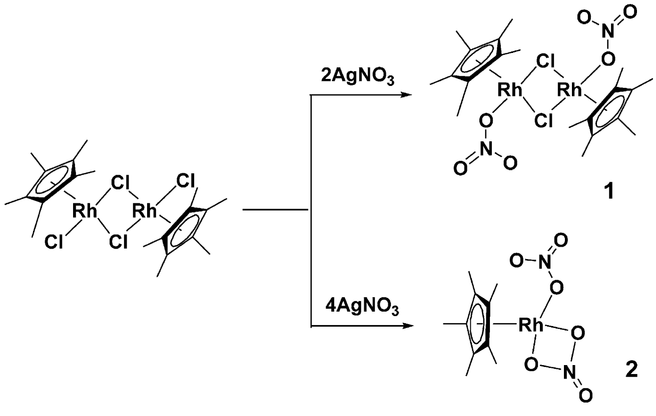
All compounds (**1**–**7**) in this study are air-stable both in solution and in the solid state. An 18-electron, dinuclear compound $[Cp^*RhCl_2]_2$ reacts with the stoichiometric amount of $AgNO_3$ (2 equiv. for **1** and 4 equiv. for **2**) in a mixed solvent of acetone and

Table 1
X-ray data collection and structure refinement

	1	**3**·2H_2O	**4**	**5**	**6**·H_2O	**7**·0.5H_2O
Formula	$C_{20}H_{30}Cl_2N_2O_6Rh_2$	$C_{70}H_{84}Cl_2N_4O_7P_2Rh_2$	$C_{20}H_{30}N_8O_6Rh_2$	$C_{11}H_{15}F_3NO_6SRh$	$C_{54}H_{50}N_3O_4P_2Rh$	$C_{20}H_{31}F_6N_5O_{4.5}PRh_2$
fw	671.18	1432.07	684.34	449.21	969.82	764.29
Temperature (K)	296(2)	296(2)	295(2)	295(2)	296(2)	296(2)
Crystal system	monoclinic	triclinic	othorhombic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P1$	$Pbca$	$P2_1/n$	$P1$	$P\bar{1}$
a (Å)	8.3874(5)	10.319(1)	14.454(3)	7.4528(6)	9.359(2)	12.9148(9)
b (Å)	10.4549(6)	10.558(1)	12.472(3)	13.4580(9)	11.098(2)	14.7295(9)
c (Å)	14.8585(9)	17.371(1)	14.767(3)	16.9124(14)	12.374(2)	15.9260(15)
α (°)		97.011(8)			73.71(1)	74.367(6)
β (°)	104.385(5)	94.348(11)		102.344(7)	71.41(1)	81.960(5)
γ (°)		112.154(6)			80.67(1)	88.816(5)
V (Å^3)	1262.1(1)	1724.5(3)	2662(1)	1657.1(2)	1165.5(3)	2888.4(4)
Z	2	1	4	4	1	4
d_{calc} (g cm^{-3})	1.766	1.379	1.707	1.801	1.382	1.758
μ (mm^{-1})	1.556	0.656	1.289	1.213	0.485	1.273
F(000)	672	742	1376	896	502	1524
T_{min}	0.6937	0.5742	0.2299	0.4048	0.4171	0.3664
T_{max}	0.9126	0.8705	0.2865	0.7977	0.4356	0.7780
2θ range (°)	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50
Scan type	ω	ω	ω	ω	ω	ω
Scan speed	variable	variable	Variable	variable	variable	variable
Number of reflections measured	2364	6401	2315	3122	4325	10 458
Number of reflections unique	2204	6401	2315	2887	4325	9990
Number of reflections with $I > 2\sigma(I)$	2062	5715	2074	2725	3912	8552
Number of parameters refined	146	797	164	209	562	703
Max., in $\Delta\rho$ (e Å^{-3})	0.298	0.603	0.373	0.372	0.289	1.449
Min., in $\Delta\rho$ (e Å^{-3})	−0.300	−0.739	−0.431	−0.572	−0.389	−0.603
GOF on F^2	1.027	1.050	1.047	1.066	1.030	1.041
R_1 [a]	0.0298	0.0347	0.0272	0.0273	0.0297	0.0431
WR_2 [b]	0.0623	0.0897	0.0733	0.0730	0.0722	0.1129

[a] $R_1 = \Sigma||F_o|-|F_c||\Sigma|F_o|$.
[b] $wR_2 = \Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

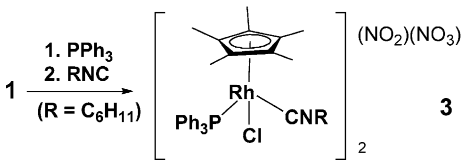
dichloromethane at room temperature to give a dinuclear Rh(III) compound, [Cp*Rh(η^1-NO_3)(μ-Cl)]$_2$ (**1**), and a mononuclear Rh(III) compound, [Cp*Rh(η^1-NO_3)(η^2-NO_3)] (**2**), in high isolation yields (96.4 and 93.1%, respectively) (Scheme 2).



Scheme 2.

The Rh metal in compounds **1** and **2** has a formal electron count of 18. Compound **2** was previously prepared by stirring [Cp*Rh(N_3)$_2$]$_2$ in nitrogen tetraoxide (N_2O_4) [17], and its crystal structure was reported by Hursthouse and co-workers [18]. Therefore, the structure of compound **2** could be confirmed by comparing its spectral and crystallographic data with those for the genuine compound. In ^{1}H NMR spectra, the Cp* methyl protons of compound **1** appear as a singlet at δ 1.61 ppm, which suggests a high molecular symmetry. In IR spectra of **1**, the bands at 1458 and 1382 cm^{-1} can be assigned to the N–O stretching.

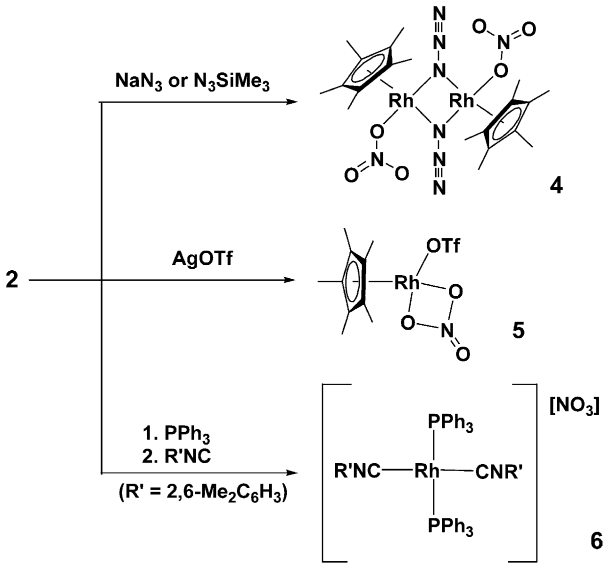
Compound **3** is prepared by the stepwise addition of two ligands to compound **1**. In the first step, PPh_3 is added to compound **1** in dichloromethane, and the solution is stirred for 3 h. In the second step, cyclohexyl isocyanide is added, and the resultant solution is stirred further for 3 h to give a chiral compound, [Cp*RhCl(PPh_3)(CN–C_6H_{11})]$_2$(NO_2)(NO_3) (**3**) in 90.4% yield (Eq. (1)).



(1)

We speculate that compound **1** converts from a dinuclear species to a mononuclear intermediate due to the coordination of the incoming PPh_3 in the first step. In the second step, the cyclohexyl isocyanide replaces the nitrato ligand, which now acts as a counterion. Interestingly, the X-ray structure of compound **3** (see below) reveals that it has two different counter-anions, nitrate (NO_3^-) and nitrite (NO_2^-) ions. The formation of the nitrite counterion indicates the N–O bond cleavage of the nitrato ligand during the reaction. Unfortunately, we cannot explain this unusual nitrate-to-nitrite reduction. However, this phenomenon has also been observed in the preparation of compound **7** (see below). Related to the chiral compound **3**, Jones and co-workers previously reported achiral Rh-isocyanide compounds of the type $Cp^*Rh(CNR)Cl_2$ (R = t-Bu or 2,6-xylyl) from $[Cp^*RhCl_2]_2$ and CNR in tetrahydrofuran [20]. In IR spectra of **3**, the band at 2205 cm^{-1} can be assigned to the C≡N stretching.

We prepared an azido-bridged dinuclear Rh(III) compound, $[Cp^*Rh(\eta^1\text{-}NO_3)(\eta^1,\mu\text{-}N_3)]_2$ (**4**), in 89.2% yield, by treating compound **2** with excess NaN_3 (3 equiv.). Compound **4** could also be prepared from compound **2** and excess N_3SiMe_3 (3 equiv.) in 84.7% yield (Scheme 3). Compound **4** contains bridging azido and terminal η^1-NO_3 ligands. In this reaction, the incoming N_3^- has appeared to replace the η^2-NO_3 ligand, although we cannot rule out the possibility of the replacement of η^1-NO_3 followed by the (η^2-NO_3) → (η^1-NO_3) transformation. In ^1H NMR spectra of **4**, the Cp* methyl protons appear as a singlet at δ 1.61 ppm, probably due to the symmetrically bridging mode of the azido ligands. As expected, the strong IR band at 2058 cm^{-1}, assigned to the N_3 bond, is consistent with those found for azido-bridged dinuclear Rh(III) complexes [17].

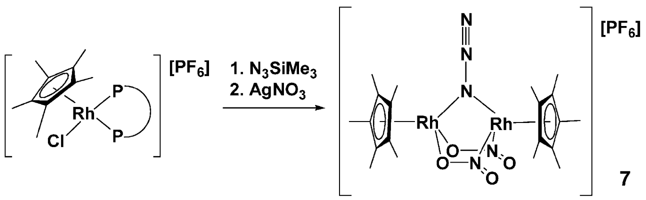


Scheme 3.

Compound **2** reacts with AgOTf in a mixed solvent of acetone and dichloromethane to give a bidentate nitrato–Rh(III) compound, $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ (**5**), in 84.7% yield (Scheme 3). Apparently, the monodentate nitrato ligand has been replaced by the incoming triflate during the reaction.

An ionic compound, *trans*-$\{[Rh(PPh_3)_2(CN\text{–}2,6\text{-}Me_2C_6H_3)_2](NO_3)\}\cdot H_2O$ (**6**·H_2O), has been prepared by the two-step addition of PPh_3 and 2,6-dimethylphenyl isocyanide to compound **2** (Scheme 3). The molecular geometry has been changed from a pseudo-octahedron to a square plane during the reaction. Both nitrato ligands in compound **2** have transformed to nitrate counterions in compound **6**. In this reaction, the Rh metal has been formally reduced from +3 to +1. It is worth noting that the strongly bound Cp* ligand has been eliminated during the reaction. Unfortunately, we cannot give an explanation for the unusual stoichiometry and reactivity (Cp* group elimination and Rh metal reduction). ^1H NMR spectra of **6** display two singlets at δ 1.64 and 1.62 ppm, which indicates diastereotopic methyl protons of 2,6-dimethylphenyl isocyanide. In $^{31}P\{^1H\}$ NMR spectra of **6**, PPh_3 ligands appear as a doublet at δ 31.55 ppm ($J_{P\text{–}Rh}$ = 122 Hz), due to the coupling of the Rh metal with the equivalent P atoms. In IR spectra of **6**, the band at 2122 cm^{-1} can be assigned to the C≡N stretching.

An ionic, dinuclear Rh(III) compound, $\{[Cp_2^*Rh_2(\eta^2,\mu\text{-}NO_2\text{-}N,O)_2(\eta^1,\mu\text{-}N_3)](PF_6)\}\cdot 0.5H_2O$ (**7**·$0.5H_2O$), has been prepared by the stepwise addition of two ligands. An 18-electron, ionic compound $[Cp^*RhCl(dppf)](PF_6)$ reacts with N_3SiMe_3 in a mixed solvent of acetone and dichloromethane for 24 h, and the resultant solution is further treated with 3 equiv. of $AgNO_3$ to give compound **7** in 25.9% yield (Eq. (2)). During the reaction, the dppf ligand has been eliminated, and the mononuclear complex has been converted to the dinuclear one. On the contrary, Yamamoto and co-workers reported that $[Cp^*RhCl(dppf)](PF_6)$ reacted with excess $NaPF_6$ (5 equiv.) in the presence of excess $AgNO_3$ (10 equiv.) in acetonitrile (MeCN) to give an ionic, solvent-coordinated compound $[Cp^*Rh(dppf)(MeCN)][PF_6]_2$ [16]. In other words, the NO_3^- ion has not been incorporated into the Rh coordination sphere in their reaction. ^1H NMR spectra of **7** display four singlets at δ 1.72, 1.65, 1.63, and 1.53 ppm, which clearly indicates the Cp* groups to be inequivalent.



(2)

3.2. Structure

The molecular structure of compound **1** is shown in Fig. 1. Compound **1** has two bridging chloro and two terminal nitrato ligands. The coordination sphere of the Rh metal can be described as a distorted octahedron, if the coordination number of the Cp* ligand is taken to be three. Compound **1** has a center of symmetry, which probably explains the singlet for Cp* methyl protons in its ^{1}H NMR spectrum. The two Cp* ligands are *trans* to each other and staggered. The Rh···Rh distance in compound **1** is 3.590(4) Å.

The structure of one of the two cations in compound **3** is shown in Fig. 2. The coordination sphere of Rh can also be described as either a pseudo-octahedron or a three-legged piano stool. Interestingly, an asymmetric unit has two chemically equal cations $[Cp^*RhCl(PPh_3)(CN{-}C_6H_{11})]^+$, together with two different counterions, nitrite (NO_2^-) and nitrate (NO_3^-). The C–N–R ($R = C_6H_{11}$) ligand is essentially linear with the bond angle of 179(1)°.

The molecular structure of compound **4** is shown in Fig. 3. Compound **4** has two bridging, end-on azido and two terminal nitrato ligands. The coordination sphere of the Rh metal can be described as a distorted octahedron. The two Cp* ligands are *trans* to each other and staggered. The end-on azido ligands are essentially linear with the bond angle of 177.8(4)°. The Rh···Rh distance in compound **4** is 3.455(6) Å.

The molecular structure of compound **5** is shown in Fig. 4. The coordination sphere of Rh can be described as either a pseudo-octahedron or a three-legged piano stool. Two Rh–O bond lengths are essentially the same (Rh1–O1 = 2.183(2) Å and Rh1–O2 = 2.179(2) Å). Therefore, the nitrate ligand can be described as a symmetric, bidentate ligand.

The molecular structure of compound **6** is shown in Fig. 5. The coordination sphere of Rh can be described as a square plane, with two *trans* isocyanide and two *trans* triphenylphosphine ligands. The coordination plane, defined by C37, C46, P1, P2, and Rh1 atoms, is essentially planar with the average atomic displacement of 0.0026 Å. The NO_3^- acts as a counterion and forms an ionic intramolecular hydrogen bond of the O–H···O–NO_2^- type with the co-crystallized water: O4–H4B = 1.06 Å, O3···O4 = 2.599 Å, H4B···O3 = 1.801 Å and O4–H4B–O3 = 124.8°. The C–N–R′ ($R' = 2,6\text{-}Me_2C_6H_3$) ligands are nearly linear with the bond angles of 174(1) and 175(1)°.

The molecular structure of compound **7** is shown in Fig. 6. The coordination sphere of Rh can be described as a pseudo-octahedron. The local geometry of the Rh metal can also be described as a three-legged piano

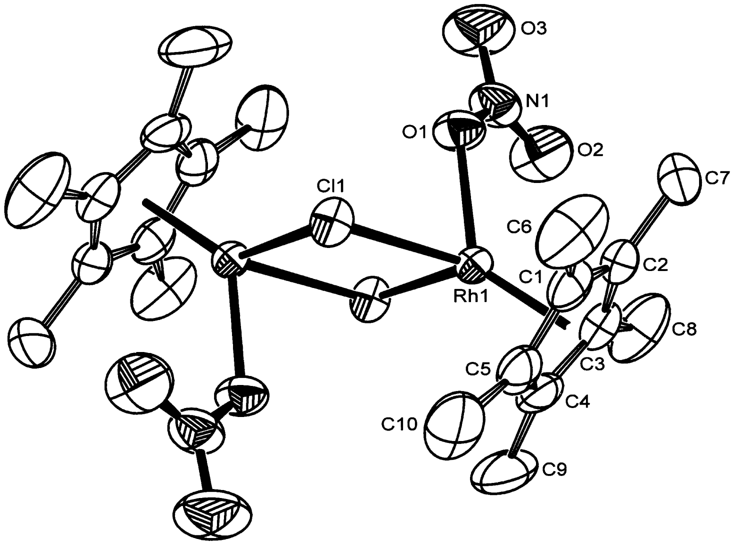


Fig. 1. ORTEP drawing of **1**, showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and bond angles (°): Rh1–O1 2.132(2), Rh1–Cl1 2.4548(7), O1–N1 1.285(3), O2–N1 1.226(4), O3–N1 1.234(4); O1–Rh1–Cl1 80.30(6), N1–O1–Rh1 122.4(2), O2–N1–O1 120.2(3), O3–N1–O1 116.3(3), O2–N1–O3 123.5(3).

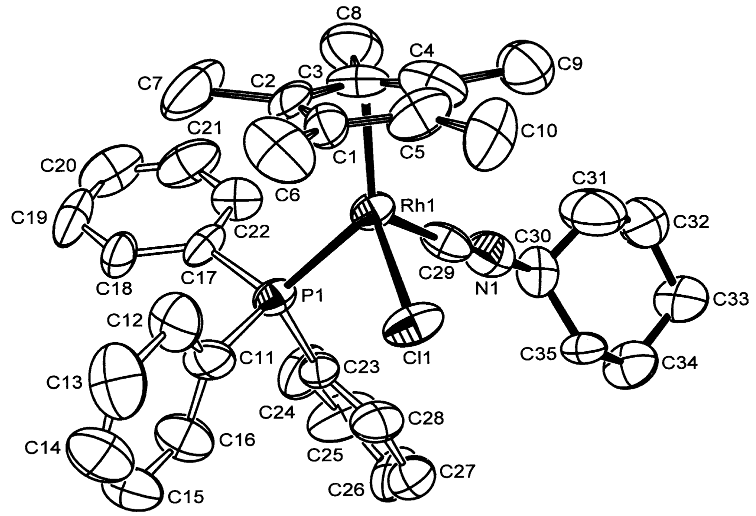


Fig. 2. ORTEP drawing of the cationic part of **3**·$2H_2O$. Selected bond lengths (Å) and bond angles (°): Rh1–C29 1.93(1), Rh1–P1 2.346(3), Rh1–Cl1 2.400(3), C29–N1 1.18(2), N1–C30 1.44(2); C29–Rh1–P1 87.6(4), C29–Rh1–Cl1 94.6(4), P1–Rh1–Cl1 88.0(1), N1–C29–Rh1 176(1), C29–N1–C30 179(1).

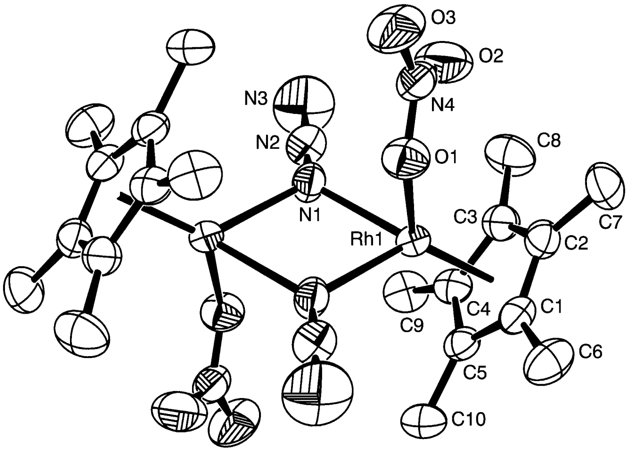


Fig. 3. ORTEP drawing of **4**. Selected bond lengths (Å) and bond angles (°): Rh1–N1 2.166(3), Rh1–O1 2.153(2), N1–N2 1.134(5), N2–N3 1.181(5), O1–N4 1.298(4), O2–N4 1.225(4), O3–N4 1.240(4); O1–Rh1–N1 85.0(1), N4–O1–Rh1 119.0(2), N1–N2–N3 177.8(4), O1–N4–O2 119.8(3), O1–N4–O3 116.6(4), O2–N4–O3 123.6(3).

stool. There are two crystallographically independent molecules in an asymmetric unit, which explains that this crystal has the *Z* value of 4 instead of 2. These two molecules are chemically equal. The $Rh_2(NO_2)_2$ core adopts a boat form, in which the dihedral angle between Plane 1 (O1, N4, O3, and N5) and Plane 2 (Rh1, N4, and N5) is 46.4(2)°, and that between Plane 1 and 3 (Rh2, O1, and O3) is 44.9(2)°, together with the dihedral angle of 88.8(2)° between Planes 2 and 3. As expected, the N–O bond distances (1.285(5) and 1.289(5) Å) in the boat framework are longer than the *exo* N–O bond lengths (1.215(6) and 1.219(6) Å). Two Rh–N (N_3) bond lengths are essentially the same (Rh1–N1 = 2.113(4) Å and Rh2–N1 = 2.116(4) Å). The end-on azido ligand is almost linear with the N–N–N bond angle of 178(1)°, and the difference between the two N–N bond lengths is 0.039 Å. The Rh···Rh distance in compound **7** is 3.478(1) Å.

The NO_2^- ion can behave as a nitrogen-donor ligand to form nitro compounds ($L_nM{-}NO_2$) or as an oxygen-donor ligand to form nitrito compounds ($L_nM{-}ONO$). Several bonding modes of the NO_2^- ligand are shown in Chart 1 [21]. The NO_2^- ligand in compound **7** belongs to the bridging type **E**.

3.3. N–O bond cleavage of NO_3^- to NO_2^-

The reduction of a nitrate ion (NO_3^-) is interesting in probing reduction processes of nitrogen oxides in nature [22]. Compounds **3** and **7** show a formal reduction of the nitrato ligand. The molecular structure of compound **3** suggests that one of the nitrato ligands has been converted to the nitrite ion (NO_2^-) by oxygen dissociation. Although we cannot explain how this conversion occurs, the X-ray structure of compound **3** definitely shows the nitrate-to-nitrite reduction. The molecular structure of $[Cp^*_2Rh_2(\eta^2,\mu\text{-}NO_2\text{-}N,O)_2(\eta^1,\mu\text{-}N_3)](PF_6)$ (**7**) also suggests the formal reduction of the nitrato ligand to the nitro ligand. Both NO_2^- ligands in compound **7** exhibit an asymmetrically bridging mode of ($\eta^2,\mu\text{-}NO_2\text{-}N,O$).

Because various oxidation states of nitrogen are available, the reduction of NO_3^- generates several products, including NO_2^-, NO, NH_3, and NH_4^+ depending on reaction conditions [23,24]. In particular,

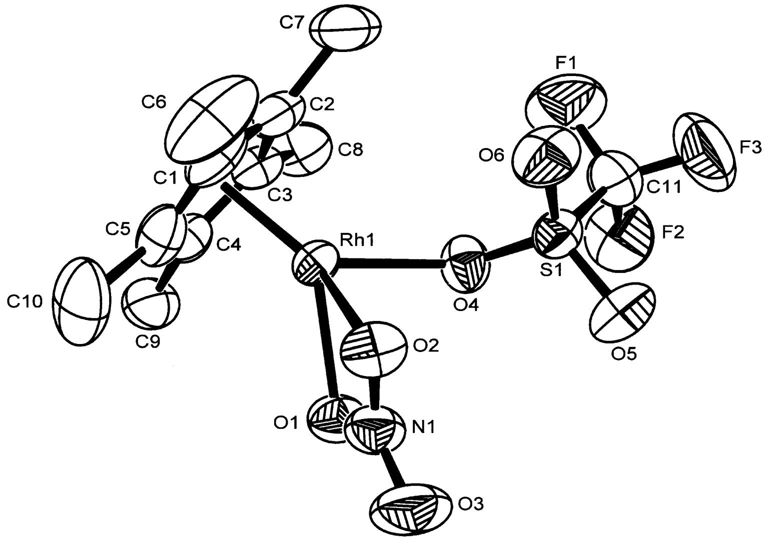


Fig. 4. ORTEP drawing of **5**. Selected bond lengths (Å) and bond angles (°): Rh1–O1 2.183(2), Rh1–O2 2.179(2), Rh1–O4 2.153(2), O1–N1 1.264(4), O2–N1 1.282(4), O3–N1 1.208(4); S1–O4–Rh1 128.35(13), O2–Rh1–O1 58.84(9), N1–O1–Rh1 93.28(17), N1–O2–Rh1 92.94(17).

Ogo and co-workers very recently reported a unique pH-dependent H_2-activation cycle that is coupled to the reduction of the nitrate ion. On the basis of ^{1}H NMR, NO_x gas analysis, and mass spectra, they proposed that, at pH = −1, the oxidation of the hydrido ligands of $[(Cp^*Ir)_2(\mu\text{-}H)_3](NO_3)$ couples to the reduction of NO_3^- ($NO_3^- \rightarrow NO_2^- \rightarrow NO$) (Eq. (3)) [25]. To our best knowledge, compounds **3** and **7** show unprecedented examples of the nitrato-to-nitro reduction in the rhodium coordination sphere. It is worth noting that the N–O bond cleavage of the nitrato ligand appears to occur only in the reactions that involve phosphine (PPh_3

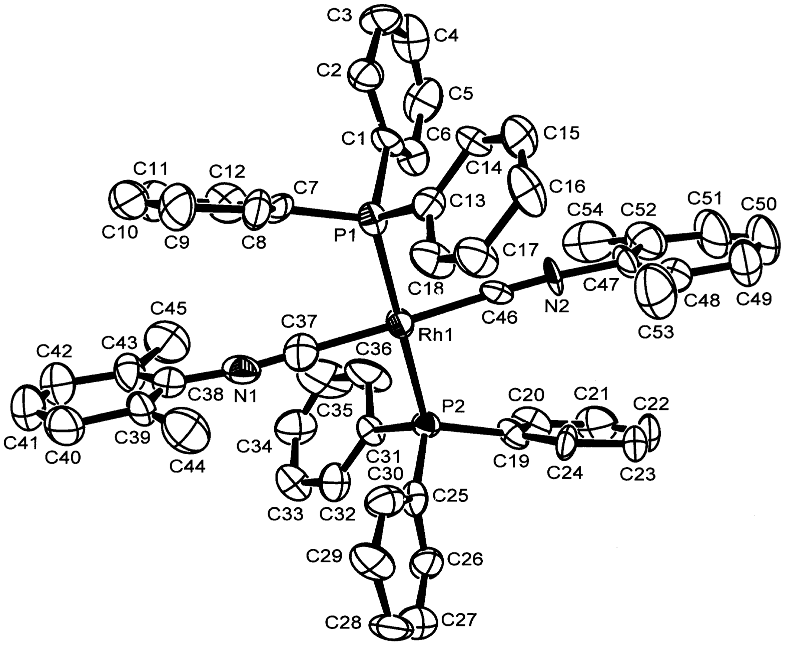


Fig. 5. ORTEP drawing of the cationic part of compound **6**·H_2O. Selected bond lengths (Å) and bond angles (°): Rh1–C37 1.93(1), Rh1–C46 1.94(1), Rh1–P1 2.274(3), Rh1–P2 2.309(3), N1–C46 1.12(1), N2–C47 1.42(1); C46–Rh1–C37 178.8(7), C46–Rh1–P1 88.6(4), C46–Rh1–P2 91.6(3), C37–Rh1–P1 90.9(4), C37–Rh1–P2 88.9(4), P1–Rh1–P2 179.8(2) C37–N1–C38 174(1), C46–N2–C47 175(1), N1–C37–Rh1 178(1), N2–C46–Rh1 178(1).

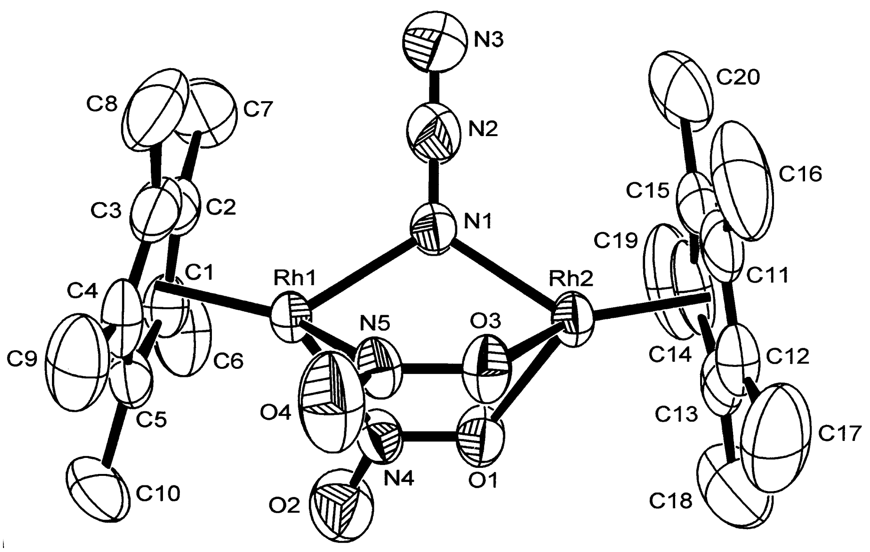


Fig. 6. ORTEP drawing of the cationic part of compound **7**$\cdot 0.5H_2O$. Selected bond lengths (Å) and bond angles (°): Rh1–N1 2.113(4), Rh1–N4 2.117(4), Rh1–N5 2.107(4), Rh2–N1 2.116(4), Rh2–O1 2.124(4), Rh2–O3 2.130(4), O1–N4 1.289(5), O2–N4 1.215(6), O3–N5 1.285(5), O4–N5 1.219(6), N1–N2 1.186(7), N2–N3 1.147(9); Rh1–N1–Rh2 110.6(2), N1–Rh1–N4 83.1(2), N1–Rh1–N5 82.6(2), N4–Rh1–N5 84.4(2), O1–N4–Rh1 121.7(3), O3–N5–Rh1 122.0(0) N1–Rh2–O1 82.8(2), N1–Rh2–O3 82.5(2), O1–Rh2–O3 85.5(2), N4–O1–Rh2 120.3(3), N5–O3–Rh2 120.4(3), N1–N2–N3 178(1).

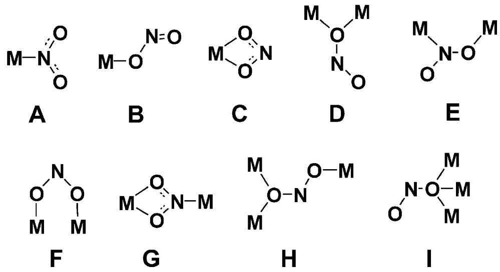


Chart 1.

or dppf). Therefore, we speculate that the phosphine plays a certain role (for example, an oxygen abstractor) in this type of reduction.

$$[(Cp^*Ir)_2(\mu\text{-}H)_3](NO_3) + 3NO_3^- \rightarrow 2[Cp^*Ir(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)] + H_2 + H^+ + 4e^- \quad (3)$$

4. Conclusions

We have prepared several nitrato- or nitro-rhodium compounds and determined their structures by X-ray diffraction. Compounds **1** and **2** were prepared by treating $[Cp^*RhCl_2]_2$ with $AgNO_3$ in different mole ratios. In particular, X-ray structures of the ionic compounds **3** and **7** reveals an unusual nitrate-to-nitrite conversion through the formal oxygen dissociation of NO_3^-. Compounds **1**, **2**, **4**, and **5** show η^1 or η^2 bonding modes of the nitrato ligand.

5. Supporting material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: CCDC No. 185913 for **1**, 185914 for **3**$\cdot 2H_2O$, 185915 for **4**, 185916 for **5**, 185917 for **6**$\cdot H_2O$, and 185918 for compound **7**$\cdot 0.5H_2O$. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] B.J. Hathaway, in: R.D. Gillard, J.A. McClevery, G. Wilkinson (Eds.), Comprehensive Coordination Chemistry, vol. 8, Pergamon Press, Oxford, 1987, pp. 413–434.

[2] C. Kimblin, V.J. Murphy, T. Hascall, B.M. Bridgewater, J.B. Bonanno, G. Parkin, Inorg. Chem. 39 (2000) 967.

[3] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fourth ed., Wiley-Interscience, New York, 1980, pp. 407–482.

[4] E.I. Eweka, D.H. Kerridge, Thermochim. Acta 290 (1996) 133.

[5] H. Nagao, K. Ito, N. Tsuboya, D. Ooyama, N. Nagao, F.S. Howell, M. Mukaida, Inorg. Chim. Acta 290 (1999) 113.

[6] M. Brönstrup, D. Schröder, I. Kretzschmar, H. Schwarz, J.N. Harvey, J. Am. Chem. Soc. 123 (2001) 142.

[7] P.A. Dimas, R.J. Lawson, J.R. Shapley, Inorg. Chem. 20 (1981) 281.

[8] (a) Y.-Q. Zheng, L.-X. Zhou, J.-L. Lin, S.-W. Zhang, Z. Anorg. Allg. Chem. 627 (2001) 1643.;
(b) C.D. Auwer, M.C. Charbonnel, M.G.B. Drew, M. Grigoriev, M.J. Hudson, P.B. Iveson, C. Madic, M. Nierllich, M.T. Presson, R. Revel, M.L. Russell, P. Thuery, Inorg. Chem. 39 (2000) 1487;
(c) A. Möller, N. Scott, G. Meyer, G.B. Deacon, Z. Anorg. Allg. Chem. 625 (1999) 181;
(d) R. Keuleers, G.S. Papaefstathiou, C.P. Raptopoulou, V. Tangoulis, H.O. Desseyn, S.P. Perlepes, Inorg. Chem. Commun. 2 (1999) 472;
(e) J.-P.M. Louloudi, V. Nastopoulos, S. Gourbatsis, S.P. Perlepes, N. Hadjiliadis, Inorg. Chem. Commun. 2 (1999) 479;
(f) A. Damiano, V. Munyejabo, M. Postel, Polyhedron 14 (1995) 1229;
(g) C. Pettinari, G.G. Lobbia, G. Sclavi, D. Leonesi, M. Colapietro, G. Portalone, Polyhedron 14 (1995) 1709;
(h) K.J. Catalan, S. Jackson, J.D. Zubkowski, D.L. Perry, E.J. Valente, L.A. Feliu, A. Polanco, Polyhedron 14 (1995) 2165;
(i) J.C. Fanning, X. Wang, A.E. Koziol, G.J. Palenik, Inorg. Chim. Acta 232 (1995) 199.

[9] G.-L. Julia, S. Mercedes, J.-V. Folgado, E. Emilio, G.-G. Santiago, B. Abarca, R. Ballesterros, Polyhedron 15 (1996) 3481.

[10] (a) S.A. Komaei, G.A.V. Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Eur. J. Inorg. Chem. (1998) 1577.;
(b) R. Ballesteros, B. Abarca, A. Samadi, S.-C. Juan, E. Emilio, Polyhedron 18 (1999) 3129;
(c) M. Tiliakos, P. Cordopatis, A. Terzis, C.P. Raptopoulou, S.P. Perlepes, E. Manessi-Zoupa, Polyhedron 20 (2001) 2203;
(d) S.C. Chan, L.L. Koh, P.-H. Leung, J.D. Ranford, K.Y. Sim, Inorg. Chim. Acta 236 (1995) 101;
(e) R.J. Anderson, P.H. Hagback, P.J. Steel, Inorg. Chim. Acta 284 (1999) 273.

[11] M.A. Romero, J.M. Salas, M. Quirós, M.P. Sánchez, J. Molina, J.E. Bahraoui, R.J. Faure, Mol. Struc. 354 (1995) 189.

[12] C.A. Bolos, P.C. Christidis, S.T. Triantafyllou, Polyhedron 17 (1998) 2719.

[13] G. Aromí, S. Bhaduri, P. Artús, K. Folting, G. Christou, Inorg. Chem. 41 (2002) 805.

[14] (a) D.D. Heinrich, K. Folting, W.E. Streib, J.C. Huffman, G. Christou, J. Chem. Soc., Chem. Commun. (1989) 1411.;
(b) S. Arrowsmith, M.F.A. Dove, N. Logan, M.Y. Antipin, J. Chem. Soc., Chem. Commun. (1995) 627.;
(c) G.B. Karet, Z. Sun, D.D. Heinrich, J.K. McCusker, K. Folting, W.E. Streib, J.C. Huffman, D.N. Hendrickson, G. Christou, Inorg. Chem. 35 (1996) 6450.

[15] J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970.

[16] J.-F. Ma, Y. Yamamoto, J. Organomet. Chem. 574 (1999) 148.

[17] W. Rigby, P.M. Bailey, J.A. McCleverty, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1979) 371.

[18] M.B. Hursthouse, K.M.A. Malik, D.M.P. Mingos, S.D. Willoughby, J. Organomet. Chem. 192 (1980) 235.

[19] SHELXTL, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1997.

[20] W.D. Jones, R.P. Duttweiler, Jr., F.J. Feher, Inorg. Chem. 29 (1990) 1505.

[21] M.A. Hitchman, G.L. Rowbottom, Coord. Chem. Rev. 42 (1982) 55.

[22] I. Willner, N. Lapidot, A. Riklin, J. Am. Chem. Soc. 111 (1989) 1883 (and references therein).

[23] J.D. Lee, Concise Inorganic Chemistry, fourth ed., Chapman & Hall, London, 1994, pp. 504–507.

[24] D.F. Shriver, P.W. Atkins, C.H. Langford, Inorganic Chemistry, Oxford University Press, Oxford, 1990, pp. 377–380.

[25] S. Ogo, H. Nakai, Y. Watanabe, J. Am. Chem. Soc. 124 (2002) 597.