Reactivity of $[Cp*Rh(\eta^2-NO_3)(CF_3SO_3)]$ toward Organic Thiols and Cyanate: Preparation and Structures of $[Cp*Rh(\mu-R)_3Cp*Rh](CF_3SO_3)$ (R = Ph, i-Bu, or Allyl) and $[Cp*Rh(\eta^1-NO_3)(\mu-NCO)]_2$

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Coordination chemistry of nitrate (NO₃) and triflate (CF₃SO₃) anions has received considerable and widespread attractions because of various bonding modes and counteranion characteristics in their metal compounds.¹ A number of studies on the preparation, structure, and property have been reported for the metal-nitrate (M-ONO₂) and metal-triflate (M-OSO₂CF₃) complexes, but few studies have been reported for the [M(ONO₂)(OSO₂CF₃)]-type complexes that possess both anionic ligands.²³

Recently, we reported the preparation and structure of $[Cp*Rh(\eta^2-NO_3)(OTf)]$ ($Cp* = C_5Mc_5$; $OTf = CF_3SO_3$) (1) prepared from $[Cp*Rh(\eta^1-NO_3)(\eta^2-NO_3)]$ and AgOTf by substitution, which possesses two labile ligands (NO_3 and OTf) in a single rhodium center.⁴ In order to investigate the reactivity of compound 1 toward organic thiols and cyanate, we treated 1 with thiophenol (C_6H_5SH), 2-methyl-1-propanethiol (Me_2CHCH_2SH), 2-propene-1-thiol ($H_2C=CH-CH_2SH$), and trimethylsilyl isocyanate (Me_3SiNCO). Herein, we report the preparation and structures of $[Cp*Rh(\mu-SR)_3Cp*Rh](OTf)$ {R = Ph (2); *i*-Bu (3); allyl (4)} and [$Cp*Rh(\eta^1-NO_3)(\mu-NCO)$]₂ (5).

Experimental Section

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon at room temperature. [Cp*Rh(η^2 -NO₃)(OTI)] (1), (η^2 nitrato)(pentamethyleyclopentadienyl)(trifluoromethanesulfonato)rhodium(III), was prepared by the literature method.⁴ All products were prepared in a similar way and recrystallized from either dichloromethane-pentane or dichloromethanehexane.

¹H-, and ¹³C{¹H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer. IR spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of [Cp*Rh(\mu-SPh)₃Cp*Rh](OTf) (2). To an orange compound 1 (100 mg, 0.22 mmol) in acetone (20 mL) was added neat thiophenol (C₆H₅SH, 0.069 mL, 0.66 mmol). The reaction mixture was stirred for 24 h, and then

the solvent was removed under vacuum. The resultant red solids were washed with hexane (10 mL × 2) and diethyl ether (10 mL × 2), and then the solvent was removed under vacuum to give orange-red crystals of **2**. (92 mg. 0.097 mmol, 87%), ¹H-NMR (CDCl₃); δ 7.81-7.33 (15H, in, SPh), 1.33 (30H, s, CsMe₃), ¹³C{¹H}-NMR (CDCl₃); δ 133.5-129.0 (Ph), 98.1 (d, J_{Rb-C} = 6.4 Hz, CsMe₅), 8.89 (s, CsMe₅). Anal. Calcd for C₃₉H₄₅F₃O₃Rh₂S₄ (M_r = 952.81); C, 49.16; H, 4.76; S, 13.46, Found; C, 49.26; H, 4.83; S, 13.29, mp; 280-282 °C (dec), IR (KBr); 3055, 2963, 2915, 1632, 1575, 1472, 1441, 1381, 1270, 1146, 1027, 636 cm⁻¹.

Preparation of [Cp*Rh(μ-S-i-Bu)₃Cp*Rh](OTf) (3). Compound 1 (100 mg, 0.22 mmol) and 2-methyl-1-propanethiol (Me₂CHCH₂SH, 0.072 mL, 0.66 mmol) were stirred to give orange-red crystals of **3**. (83 mg, 0.085 mmol, 76%). ¹H-NMR (CDCl₃): δ2.28 (6H, d, $J_{H,H} = 11.5$ Hz, SCH₂CHMe₂), 1.73 (30H, s. CsMe₅), 1.70 (3H, m, SCH₂CHMe₂), 1.12 (18H, d, $J_{H,H} = 11.0$ Hz, SCH₂CHMe₂), ¹³C (¹H)-NMR (CDCl₃): δ 98.0 (d, $J_{Rh,C} = 10.9$ Hz, C_5Me_5), 42.0 (s. SCH₂CHMe₂), 32.2 (s. SCH₂CHMe₂), 22.5 (s. SCH₂CHMe₂), 9.7 (s. CsMe₅), Anal. Calcd for C₃₄H₅₉Cl₂F₃O₃Rh₂S₄ ($M_r = 977.77$): C. 41.76; H, 6.08; S, 13.12, Found: C, 42.28; H, 6.20; S, 13.21, mp; 236-238 °C, IR (KBr); 2960, 2924, 2870, 1635, 1461, 1380, 1271, 1226, 1148, 1074, 1029, 638 cm⁻¹.

Preparation of [Cp*Rh(\mu-S-allyl)₃Cp*Rh](OTf) (4). Compound 1 (100 mg, 0.22 mmol) and 2-propene-1-thiol (H₂C=CHCH₂SH, 0.056 mL, 0.66 mmol) were stirred to give orange-red crystals of 4. (77 mg, 0.091 mmol, 82%). ¹H-NMR (CDCl₃): δ 2.37 (6H, m, SCH₂CHCH₂), 1.74 (30H, s, C₃Me₅), 1.69 (3H, m, SCH₂CHCH₂), 1.05 (6H, m, SCH₂CH(*H*₂), ¹³C{¹H}-NMR (CDCl₃): δ 97.89 (d, J_{Rh-C} = 6.4 Hz, C₃Me₅), 34.91 (s, SCH₂CHCH₂), 27.50 (s, SCH₂C'H-CH₂), 13.94 (s, SCH₂CHC'H₂), 9.50 (s, C₃Me₅). Anal. Calcd for C₃₀H₄sF₃O₃Rh₂S₄ (M_r = 844.72); C, 42.65; H, 5.37; S, 15.18. Found: C, 42.48; H, 5.24; S, 15.08, mp; 276-278 °C (dec.), IR (KBr): 2965, 2924, 2873, 1630, 1459, 1381, 1269, 1222, 1146, 1084, 1026, 636 cm⁻¹.

Preparation of [Cp*Rh(η^{1} -**NO**₃)(μ -**NCO**)]₂ (5). Compound 1 (100 mg. 0.22 mmol) and trimethylsily1 isocyanate (Me₃SiNCO, 0.089 mL, 0.66 mmol) were stirred to give orange-red crystals of 5. (66 mg, 0.097 mmol, 87%). ¹H-NMR (CDCl₃): δ 1.62 (30H, s. C₃*Me*₅). ¹³C{¹H}-NMR (CDCl₃): δ 93.94 (d. *J*_{Rh-C} = 9.7 Hz, C₅Me₅), 8.70 (s. C₅*Me*₅). Anal. Calcd for C₂₂H₃₀N₄O₈Rh₂ (*M*_r = 684.32); C. 38.61; H,

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Table 1. X-ray data collection and structure refinement

	2	$3 \cdot CH_2Cl_2$	4	5
empirical formula	$C_{39}H_{45}F_3O_3Rh_2S_4$	C34H59Cl2F3O3Rh2S4	C30H45F3O3Rh2S4	C22H30N4O8Rh2
fw	952.81	977.77	844.72	684.32
temperature. K	293(2)	295(2)	293(2)	293(2)
crystal system	trielinie	monoclinic	trielinie	orthorhombie
space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	Pbca
a, Å	11.622(2)	11.076(2)	10.906(3)	14.497(3)
5. Å	12.473(3)	19.427(3)	12.467(3)	12.379(3)
с, Å	16.321(4)	20.630(3)	14.276(3)	14.677(4)
a, deg	78.80(1)		102.13(1)	
B, deg	74.36(5)	98.07(1)	98.44(2)	
χ deg	62.64(2)		97.36(2)	
V. Å ³	2016.5(8)	4395(1)	1851.6(8)	2634(1)
<u>.</u>	2	4	2	4
l_{cal} , g cm ⁻³	1.569	1.478	1.515	1.726
$u_{\rm a} {\rm mm}^{-1}$	1.075	1.105	1.159	1.305
F(000)	968	2008	860	1376
T _{min}	0.5232	0.6775	0.6612	0.2378
Tmax	0.5578	0.9072	0.9017	0.2694
2θ range (°)	3.5-50	3.5-50	3.5-50	3.5-50
scan type	ω	ω	ω	ω
sean speed	variable	variable	variable	variable
No. of refins measured	7316	7597	6732	2326
No. of refins unique	6943	7590	6371	2326
No. of reflues with $I = 2\sigma(I)$	3890	5790	4197	1401
No. of params refined	489	461	407	164
Max., in $\Delta \rho$ (e Å ⁻³)	0.603	0.543	0.578	0.510
Min., in $\Delta \rho$ (e Å ⁻³)	-0.744	-0.499	-0.510	-0.493
$GOF \text{ on } F^2$	1.008	1.017	1.045	0.966
R	0.0680	0.0533	0.0541	0.0475
wRz ^o	0.1267	0.1225	0.1316	0.0924

 ${}^{\mu}wR_{2} = \Sigma [w(F_{o}{}^{2} - F_{c}{}^{2})^{2}] \Sigma [w(F_{o}{}^{2})^{2}]^{1/2}.$

4.42; N, 8.19. Found: C, 38.53; H, 4.34; N, 8.12. mp; 228-230 °C (dec.). IR (KBr): 2964, 2919, 2167, 1631, 1460, 1383, 1279, 1161, 1084, 1022, 804, 643 cm⁻¹.

X-ray structure determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and intensity data are shown in Table 1. Intensity data were empirically corrected for absorption with ψ -scan data. All calculations were carried out with the use of SHELXTL programs.⁵

An orange-red crystal of **2**, shaped as a block of approximate dimensions $0.16 \times 0.14 \times 0.12$ mm, was used for crystal- and intensity-data collection. The unit-cell parameters suggested a triclinic lattice, and successful structural convergence was obtained in the centrosymmetric space group $P\overline{1}$. An orange-red crystal of **3**, shaped as a block of approximate dimensions $0.30 \times 0.20 \times 0.18$ mm, was used. The unit-cell parameters and systematic absences. h0l (l = 2n + 1) and 0k0 (k = 2n + 1), unambiguously indicated $P2_1/c$ as a space group. An orange-red crystal of **4**, shaped as a block of approximate dimensions $0.20 \times 0.18 \times 0.16$ mm, was used. The unit-cell parameters suggested a triclinic lattice, and successful structural convergence was obtained in the

centrosymmetric space group $P\overline{1}$. An orange-red crystal of 5. shaped as a block of approximate dimensions $0.12 \times 0.10 \times 0.08$ mm, was used. The unit-cell parameters and systematic absences, 0kl (k = 2n + 1). h0l (l = 2n + 1), and hk0 (h = 2n + 1). unambiguously indicated Pbca as a space group. All structures were solved by direct methods. All non-hydrogen atoms were generated in ideal positions and refined in a riding model. The sulfur atoms of the thiolato ligands in 2-4 exhibited a structural disorder, and the best fit was obtained by considering those atoms to be distributed over two positions with the site occupation factor of 0.63:0.37 (for 2), 0.67:0.33 (for 3), or 0.67:0.33 (for 4). Selected bond lengths and bond angles are shown in Table 2.

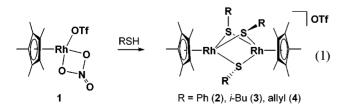
Results and Discussion

Preparation. All products are air-stable both in solution and in the solid state. Each compound is an orange-red crystal and has been fully characterized by spectroscopy $({}^{1}\text{H}, {}^{13}\text{C}{}^{1}\text{H}$ }-NMR, and IR), elemental analysis, and X-ray diffraction. Notes

Table 2. Selected bond lengths (Å) and bond angles (°)

Compound 2	:				
Rh1-S1	2.410(4)	Rh1-S2	2.373(4)	Rh1-S3	2.447(4)
Rh2-S1	2.354(4)	Rh2-82	2.375(4)	Rh2-83	2.419(4)
Rh1-S1-Rh2	86.0(1)	Rh1-S2-Rh2	86.3(1)	Rh1-S3-Rh2	83.8(1)
S1-Rh1-S2	79.1(1)	S1-Rh1-S3	78.7(1)	S2-Rh1-S3	77.9(1)
S1-Rh2-S2	80.2(1)	S1-Rh2-S3	80.3(1)	S2-Rh2-S3	78.4(1)
Compound 3					
Rh1-S1	2.398(2)	Rh1-S2	2.406(3)	Rh1-S3	2.396(3)
Rh2-S1	2.388(2)	Rh2-82	2.368(2)	Rh2-83	2.362(3)
Rh1-S1-Rh2	85.42(8)	Rh1-S2-Rh2	85.67(8)	Rh1-S3-Rh2	86.05(8)
S1-Rh1-S2	78.42(8)	S1-Rh1-S3	78.15(9)	S2-Rh1-S3	78.26(8)
S1-Rh2-S2	79.35(9)	S1-Rh2-S3	79.01(9)	S2-Rh2-S3	79.70(9)
Compound 4					
Rh1-S1	2.386(3)	Rh1-S2	2.401(2)	Rh1-S3	2.375(3)
Rh2-S1	2.385(3)	Rh2-82	2.384(3)	Rh2-S3	2.361(3)
Rh1-S1-Rh2	85.73(9)	Rh1-S2-Rh2	85.44(8)	Rh1-S3-Rh2	86.53(9)
S1-Rh1-S2	77.57(9)	S1-Rh1-S3	79.4(1)	S2-Rh1-S3	78.41(9)
S1-Rh2-S2	77.91(9)	S1-Rh2-S3	79.7(1)	S2-Rh2-S3	79.00(9)
Compound 5					
Rh1-N2	2.172(6)	Rh1-O1	2.151(5)	N2-C11	1.161(9)
C11-04	1.177(9)	01-N1	1.296(8)	02-N1	1.221(8)
03-N1	1.247(9)				
OI-Rh1-N2	80.9(2)	NI-OI-RhI	120.5(5)	N2-C11-O4	179(1)
01-N1-02	119.1(8)	O1-N1-O3	118.4(7)	O2-N1-O3	122.5(8)

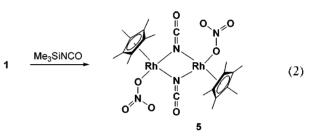
An 18-electron, mononuclear compound $|Cp*Rh(\eta^2-NO_3)|$ (OTf)] (1) reacts with excess (three equivalents) organic thiols to give triply thiolato-bridged, ionic, dinuclear rhodium(III) compounds of the type $|Cp*Rh(\mu-SR)_3Cp*$ - $Rh[(OTf) \{R = Ph(2); i-Bu(3); allvl(4)\} (eq 1).$ The nitrato and triflate ligands have been replaced by the thiolates during the reaction, suggesting their labile character. The types of the thiol employed in this study are aryl (Ph), alkyl (*i*-Bu), and allyl (H₂C=CHCH₂). The ability of thiolates to act as bridging ligands is well established, and many bimetallic compounds containing two bridging thiolato ligands have been reported.⁶² However, the rhodium compounds containing three bridging thiolato ligands are rare.⁸⁻¹¹ Furthermore, the methylthiolato (SMe) and perfluorobenzenethiolato (SC₆F₄H-p and SC₆F₅) compounds of Cp*Rh(III) or Cp*Ir(III) were previously prepared from $|Cp^*MCl_2|_2$ (M = Rh or Ir) and main-group metal thiolates $\{Pb(SR_F)_2 \text{ or NaSMe}\}^{9.11}$ By contrast, our reaction system proceeds with simple organic thiols.



The ¹H- and ¹³C{¹H}-NMR spectra of compounds **2-4** display the correct number of peaks, splittings, and intensities associated with the two components: Cp^* ligands and

thiolato ligands. In ¹H-NMR spectra of these compounds, the Cp* methyl protons appear as a singlet at δ 1.33-1.74 ppm. probably due to the symmetrically bridging mode of the thiolato ligands. It is difficult to relate the magnitude of $J_{\rm Rh-C}$ to the substitutent on the thiolato ligand (*i*-Bu > Ph \approx H₂C = CHCH₂).

We prepared a doubly cyanato-bridged dinuclear Rh(III) compound, $[Cp^*Rh(\eta^1-NO_3)(\mu-NCO)]_2$ (5), by treating compound 1 with excess (three equivalents) trimethylsilyl isocyanate (eq 2). In this reaction, the incoming NCO⁻ appears to have replaced the OTf⁻ ligand. followed by the $(\eta^2-NO_3) \rightarrow (\eta^1-NO_3)$ transformation.



In ¹H-NMR spectra of 5. the Cp* methyl protons appear as a singlet at δ 1.62 ppm, probably due to the symmetrically bridging mode of the cyanato ligands. The strong IR band at 2167 cm⁻¹, assigned to the CN bond, is consistent with those found for cyanato-bridged dinuclear Rh(III) compounds.¹²

Structure. The molecular structures of compounds **2-4** are shown in Figures 1-3. respectively. Compounds **2-4** are isostructural, and each one has three μ_2 -thiolato ligands and two Cp* ligands. The coordination sphere of each rhodium can be described as a distorted octahedron, if the coordination number of the Cp* ligand is taken to be three. In addition, the Cp* ligands coordinate to the rhodium metals in an eclipsed conformation. The Rh…Rh distances are in the range of 3.246(1)-3.248(1) Å, the Rh-S-Rh bond angles are in the range of 85.4(av.)- $85.9^{\circ}(av.)$, and the S-Rh-S bond angles are in the range of 78.7(av.)- $79.1^{\circ}(av.)$. These bonding

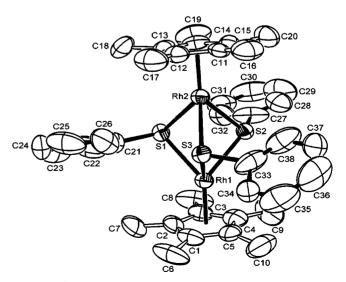


Figure 1. ORTEP drawing of **2**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

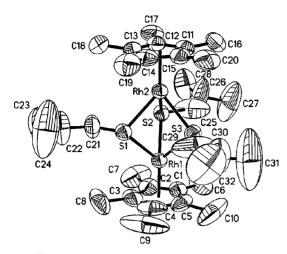


Figure 2. ORTEP drawing of 3.

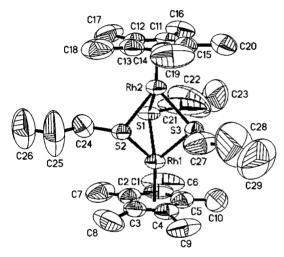


Figure 3. ORTEP drawing of 4.

parameters are similar to those found in the closely related compounds. $[Cp*Rh(\mu-SMe)_3RhCp*]_2[W_3S_9]$ and $[Cp*Rh(\mu-SC_6F_5)_3RhCp*][Cp*Rh(C_6F_5)_3]^{9+11}$

The molecular structure of compound 5 is shown in Figure 4. Compound 5 has two bridging cyanato and two terminal nitrato ligands. The coordination sphere of each rhodium can be described as a distorted octahedron. The two Cp* ligands are *trans* to each other and staggered. The cyanato ligands are essentially linear with the N-C-O bond angle of $179(1)^{\circ}$. The Rh…Rh distance in compound 5 is 3.353(1) Å.

In summary, we have prepared three triply thiolato-bridged dirhodium compounds of the type $[Cp*Rh(\mu-SR)_3Cp*Rh]$ (OTf) (R = Ph; *i*-Bu; allyl) and one doubly cyanato-bridged dirhodium compound, $[Cp*Rh(\eta^1-NO_3)(\mu-NCO)]_2$, by treating $[Cp*Rh(\eta^2-NO_3)(OTf)]$ with the corresponding organic thiols and cyanate. These results suggest that the nitrato and triflate ligands in compound **1** are labile enough to be readily

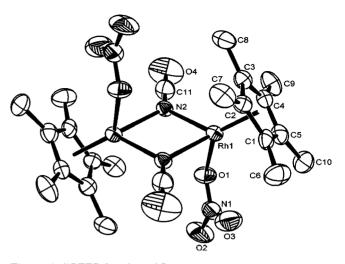


Figure 4. ORTEP drawing of 5.

replaced by organic thiols and cyanate. A further study on the reactivity of **1** is under progress.

Supplementary material. Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center. CCDC No. 191154 for **2**, 191155 for **3** °CH₂Cl₂, 191156 for **4**, and 199516 for **5**. 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: *depositiq*. *ccdc.cam.ac.uk* or *www: http://www.ccdc.cam.ac.uk*).

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Notes