

***cis, fac*-Dibromooxotris(2,6-dimethylphenyl
isocyanide)molybdenum(IV),
cis, fac-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃]의 분리 및 구조**

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**Isolation and Structure of *cis, fac*-Dibromooxotris(2,6-dimethylphenyl
isocyanide)molybdenum(IV), *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃]**

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요 약

cis, cis, trans-[MoBr₂(CO)₂(PPh₃)₂]와 2,6-dimethylphenyl isocyanide의 반응으로부터 화합물 *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃] (**1**)이 분리되었다. 화합물 **1**의 구조가 분광학적 방법(¹H-NMR, ¹³C{¹H}-NMR, IR) 및 X-ray 회절법으로 규명되었다. 화합물 **1**의 결정학 자료: 삼사정계 공간군 $P\bar{1}$, $a = 9.172(2)$ Å, $b = 11.550(3)$ Å, $c = 15.106(3)$ Å, $\alpha = 100.44(2)^\circ$, $\beta = 107.12(2)^\circ$, $\gamma = 107.83(1)^\circ$, $Z = 2$, $R(wR^2) = 0.0529(0.1344)$.

Abstract

From the reaction of *cis, cis, trans*-[MoBr₂(CO)₂(PPh₃)₂] with 2,6-dimethylphenyl isocyanide, a molybdenum oxohaloisocyanide compound *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃] (**1**) was isolated. Compound **1** was characterized by spectroscopy (¹H-NMR, ¹³C{¹H}-NMR, and IR) and X-ray diffraction. Crystallographic data for **1**: triclinic space group $P\bar{1}$, $a = 9.172(2)$ Å, $b = 11.550(3)$ Å, $c = 15.106(3)$ Å, $\alpha = 100.44(2)^\circ$, $\beta = 107.12(2)^\circ$, $\gamma = 107.83(1)^\circ$, $Z = 2$, $R(wR_2) = 0.0529(0.1344)$.

1. Introduction

Organic isocyanide complexes of transition metals are generally prepared by the ligand exchange with a free organic isocyanide,¹ electrophilic addition of an electrophile (RX) at the cyano nitrogen,^{2,3} radical alkylation of a cyanometalate with a diazonium salt,⁴ or hydroisocyanation of an olefin.⁵

Recently, our group prepared several iron(II)-organic isocyanide complexes of the type *trans*-[FeH(CNR)(dppe)₂]X, by treating *trans*-[FeH(CN)(dppe)₂] with electrophiles (RX : R = alkyl, allyl, propargyl, or aryl; X = Br, I, or O₃SCF₃).^{6,7} As a continuation of our investigation into the metal-isocyanide complexes, we set out to prepare Mo-iso-

cyanide (Mo-CNR) compounds. When we treated *cis, cis, trans*-[MoBr₂(CO)₂(PPh₃)₂] with 5 equiv of 2,6-dimethylphenyl isocyanide to obtain a tetra(isocyanide)-substituted compound *cis*-MoBr₂(CN-C₆H₃-2,6-Me₂)₄, we isolated the title compound *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃] (**1**), which might have been formed by the hydrolysis of the reaction product MoBr₂(CN-C₆H₃-2,6-Me₂)₄. We herein report on the isolation and characterization of compound **1**.

2. Experimental Section

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were

manipulated in a glove box filled with argon. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for about 48 h, neutralized with K_2CO_3 , stirred over sodium metal, and distilled by vacuum transfer. Benzene was stirred over sodium metal and distilled under argon. NMR solvent (CDCl_3) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. 2,6-Dimethylphenyl isocyanide was purchased from Fluka company. $\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2$ was prepared by the literature method.⁸⁾

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane (TMS). IR spectra were recorded with a Nicolet 205 FT-IR spectrophotometer. Melting points were measured with a Thomas Hoover capillary-melting-point apparatus without calibration.

Isolation of *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃] (1). $\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2$ (0.10 g, 0.12 mmol) and 2,6-dimethylphenyl isocyanide (0.15 g, 0.60 mmol) in benzene (30 mL) were stirred for 2 h at room temperature. The resultant orange solution was filtered, and the solvent was removed under vacuum to give orange solids. These solids were washed with diether ether (30 mL \times 2) and recrystallized from dichloromethane-hexane to give blue crystals of **1** (0.02 g, 0.03 mmol, 25%). ^1H -NMR (CDCl_3): δ 7.18~7.36 (Ph), 2.59 (CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 128.39~136.18 (Ph), 19.07 (CH_3). mp: 173~175°C. IR (KBr): 3053, 2985, 2916, 2161 (CN), 1628, 1420, 953, 895 cm^{-1} .

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. The orientation matrix and unit-cell parameters were determined by the least-squares analyses of the setting angles of 20 reflections in the range of $10.0 < 2\theta < 25.0^\circ$. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay

corrections were also made. Intensity data were corrected for absorption with Ψ -scan data. All calculations were carried out with the use of the SHELXTL programs.⁹⁾

A blue crystal of **1**, shaped as a block of approximate dimensions $0.16 \times 0.38 \times 0.18 \text{ mm}^3$, was used for crystal- and intensity-data collection. The unit-cell parameters suggested a triclinic lattice, and a successful structural convergence was obtained in the centrosymmetric space group $P\bar{1}$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode. Details on X-ray data collection and structure refinements are given in Table 1. Final atomic coordinates and some selected bond lengths and bond angles are shown in Tables 2 and 3,

Table 1. X-ray data collection and structure refinement

empirical formula	$\text{C}_{27}\text{H}_{27}\text{N}_3\text{OBr}_2\text{Mo}$
fw	665.28
temperature, K	296(2)
crystal system	triclinic
space group	$P\bar{1}$
<i>a</i> , Å	9.172(2)
<i>b</i> , Å	11.550(3)
<i>c</i> , Å	15.106(3)
α , deg	100.44(2)
β , deg	107.12(2)
γ , deg	107.83(1)
<i>V</i> , Å ³	1389.7(6)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ⁻³	1.590
μ , mm ⁻¹	3.370
<i>F</i> (000)	660
2 θ range (°)	3.5~50
scan type	ω
scan speed	variable
<i>T</i> _{min}	0.1836
<i>T</i> _{max}	0.6546
No. of reflns measured	5102
No. of reflns unique	4776
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	3988
No. of params refined	308
Max. in $\Delta\rho$ (e Å ⁻³)	2.837
Min. in $\Delta\rho$ (e Å ⁻³)	-1.021
GOF on <i>F</i> ²	1.028
<i>R</i>	0.0529
<i>wR</i> ₂ ^a	0.1344

$$^a wR_2 = [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]^{1/2}$$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Mo(1)	441(1)	730(1)	3112(1)	41(1)
Br(1)	1313(1)	1545(1)	1718(1)	63(1)
Br(2)	3347(1)	2197(1)	4371(1)	60(1)
O(1)	-412(4)	47(3)	3848(3)	36(1)
N(1)	-3064(6)	-908(5)	1288(4)	47(1)
N(2)	-420(6)	3306(4)	3405(3)	43(1)
N(3)	2246(6)	-1253(5)	2696(4)	48(1)
C(1)	-1773(7)	-313(5)	1899(4)	44(1)
C(2)	-4682(7)	-1531(5)	596(4)	42(1)
C(3)	-5813(7)	-971(6)	637(4)	47(1)
C(4)	-7399(9)	-1617(8)	-45(6)	67(2)
C(5)	-7802(9)	-2742(8)	-726(6)	74(2)
C(6)	-6673(10)	-3267(7)	-749(5)	70(2)
C(7)	-5036(8)	-2680(6)	-78(5)	54(2)
C(8)	-5297(10)	285(7)	1385(5)	63(2)
C(9)	-3713(11)	-3184(7)	-103(7)	80(2)
C(10)	-193(7)	2378(5)	3289(4)	43(1)
C(11)	-387(8)	4552(5)	3653(4)	42(1)
C(12)	-1851(9)	4702(6)	3641(4)	52(2)
C(13)	-1702(12)	5980(8)	3943(5)	71(2)
C(14)	-233(15)	6960(8)	4207(6)	84(3)
C(15)	1167(12)	6770(7)	4170(5)	71(2)
C(16)	1129(9)	5538(6)	3901(4)	51(2)
C(17)	-3426(9)	3595(8)	3350(6)	72(2)
C(18)	2629(9)	5297(7)	3880(6)	69(2)
C(19)	1556(7)	-599(6)	2810(4)	48(1)
C(20)	3119(7)	-2034(5)	2534(4)	43(1)
C(21)	2223(8)	-3218(6)	1826(5)	53(2)
C(22)	3104(9)	-3960(7)	1671(5)	61(2)
C(23)	4766(10)	-3543(7)	2191(5)	64(2)
C(24)	5606(9)	-2381(6)	2891(5)	53(2)
C(25)	4786(7)	-1583(6)	3085(4)	43(1)
C(26)	401(9)	-3633(8)	1279(6)	75(2)
C(27)	5704(8)	-313(6)	3857(5)	57(2)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

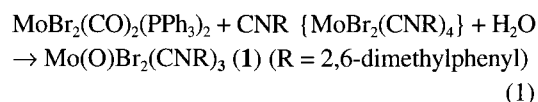
Table 3. Selected bond lengths (\AA) and bond angles ($^\circ$)

Mo1-O1	1.711(3)	Mo1-C1	2.107(6)	Mo1-C19	2.142(6)
Mo1-C10	2.150(6)	Mo1-Br2	2.584(1)	Mo1-Br1	2.684(1)
N1-C1	1.165(7)	N2-C10	1.146(7)	N3-C19	1.146(7)
N1-C2	1.405(7)	N2-C11	1.408(7)	N3-C20	1.412(7)
O1-Mo1-C1	90.9(2)	O1-Mo1-C19	96.4(2)	C1-Mo1-C19	93.8(2)
O1-Mo1-C10	98.2(2)	C1-Mo1-C10	91.2(2)	C19-Mo1-C10	164.4(2)
O1-Mo1-Br2	99.9(1)	C1-Mo1-Br2	169.3(2)	C19-Mo1-Br2	85.5(2)
C10-Mo1-Br2	86.8(2)	O1-Mo1-Br1	170.6(1)	C1-Mo1-Br1	79.8(2)
C19-Mo1-Br1	83.6(2)	C10-Mo1-Br1	82.8(2)	Br2-Mo1-Br1	89.49(3)
C1-N1-C2	173.8(6)	C10-N2-C11	169.5(6)	C19-N3-C20	177.9(6)

respectively.

3. Results and Discussion

Isolation. The title compound has been prepared by the reaction of *cis,cis,trans*-[MoBr₂(CO)₂(PPh₃)₂] with excess (5 equiv) 2,6-dimethylphenyl isocyanide in benzene. During the reaction, an initially blue slurry slowly turned to an orange solution. The solid product was recrystallized from dichloromethane-hexane to give orange crystals, whose structure has turned out to be *cis,trans*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃] (**1**), but not our target compound MoBr₂(CNR)₄ (R = 2,6-Me₂-C₆H₃). The formal oxidation state of Mo in compound **1** is +4 (d²), indicating the Mo metal has been oxidized during the reaction. We speculate that the compound **1** has been formed by the hydrolysis of the reaction product (or intermediate) MoBr₂(CNR)₄, due to the presence of a trace amount of water in the reaction mixture (eq. 1). Lippard and Novotny previously reported the synthesis and spectroscopic characterization of a cationic molybdenum(IV) oxohaloisocyanide complex of the type [(RNC)₄MoOCl]Y (R = Me, Et, or Me₃C; Y = PF₆), which is the only one precedent to our title compound in terms of molybdenum oxohaloisocyanide complexes.¹⁰



Compound **1** is air- and moisture-stable both in solution and in the solid state. The methyl protons appear at δ 2.59 ppm and phenyl protons at δ 7.18~7.36 ppm in the ¹H-NMR spectrum. The ¹³C{¹H}-

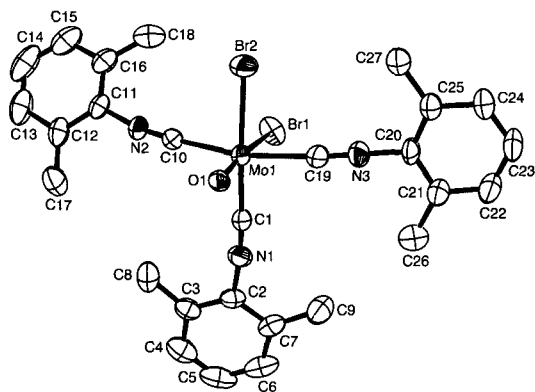


Fig. 1. An ORTEP drawing of **1** with the atom-labeling scheme and 50% probability thermal ellipsoids.

NMR spectrum displays a peak at δ 19.07 ppm for methyl carbons. In the IR spectrum, the $C\equiv N$ stretching mode appears at 2161 cm^{-1} .

Structure. The molecular structure of compound **1** is shown in Fig. 1. The coordination sphere of Mo can be described as an octahedron, with one oxo, two *cis* bromo, and three *facial* isocyanide ($CN-C_6H_3-2,6-Me_2$) ligands. The equatorial plane, defined by Mo1, Br1, Br2, C1, and O1, is relatively planar with the average atomic displacement of 0.0104 \AA .

All bond lengths and bond angles are normal within experimental errors. The bond length of Mo1-O1 of $1.711(3)\text{ \AA}$ indicates a Mo=O double bond, which falls in the range of $1.632\text{--}1.743\text{ \AA}$ found in Mo(IV) compounds.¹¹ The Mo1-Br1 bond ($2.684(1)\text{ \AA}$) *trans* to the oxo ligand (O1) is significantly longer than the Mo1-Br2 bond ($2.584(1)\text{ \AA}$) *trans* to the isocyanide ligand, which suggests a stronger *trans*-influence effect of the oxo ligand compared with the isocyanide ligand.¹²

In summary, we have structurally characterized a neutral molybdenum(IV) oxobromoisocyanide compound, *cis, fac*-[Mo(O)Br₂(CN-C₆H₃-2,6-Me₂)₃], which was isolated from the reaction of *cis, cis, trans*-[MoBr₂(CO)₂(PPh₃)₂] with 2,6-dimethylphenyl isocyanide.

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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