

Electrophilic Attack of the Phenyl Isocyanate Carbon at the Bridging Imido Nitrogen: Preparation and Structure of $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}(\mu\text{-NPh})(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$

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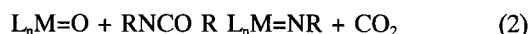
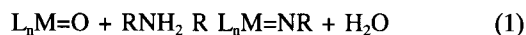
Bis(diethyldithiocarbamato)dioxomolybdenum(VI), *cis*- $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$, **1**, reacted with chlorotrimethylsilane (Me_3SiCl) to give a seven-coordinate, pentagonal bipyramidal complex $\text{MoOCl}_2(\text{S}_2\text{CNEt}_2)_2$, **3**, in which the oxo ligand is *trans* to the chloride ligand and the two chloride ligands are mutually *cis*. The monooxo molybdenum complex bis(diethyldithiocarbamato)oxomolybdenum(IV), $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$, **2**, reacted with phenyl isocyanate (PhNCO) to give an Mo dimer $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}(\mu\text{-NPh})(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$, **4**, which contains an Mo-Mo bond, two diethyldithiocarbamato ligands, two terminal imido (NPh) ligands, and two bridging imido (NPh) ligands. One of the two bridging NPh ligands seemed to have been attacked by the electrophilic phenyl isocyanate carbon, which suggests that the bridging imido NPh ligand is more nucleophilic than the terminal one. Crystallographic data for **3**: monoclinic space group $P2_1/c$, $a=8.908(1)$ Å, $b=17.509(3)$ Å, $c=12.683(2)$ Å, $\beta=110.15(1)^\circ$, $Z=4$, $R(wR_2)=0.0611(0.1385)$. Crystallographic data for **4**·THF: orthorhombic space group $P2_12_12_1$, $a=17.932(4)$ Å, $b=22.715(5)$ Å, $c=11.802(3)$ Å, $Z=4$, $R(wR_2)=0.0585(0.1286)$.

Introduction

Transition-metal imido (or nitrene, $\text{L}_n\text{M}=\text{NR}$) complexes have been of continuous interest.¹⁻⁶ They have been postulated to be important intermediates in many catalytic processes.⁷⁻⁹ The imido ligand allows stabilization of metal complexes in high oxidation states. In addition, this ligand, which has been regarded as a typically inert ligand, exhibits interesting reactivities.¹⁰

An imido ligand is isoelectronic with an oxo ligand³ and is related to a cyclopentadienyl ligand,¹¹⁻¹² an alkylidyne ligand,¹³ and an alkoxide ligand.¹⁴ All the ligands mentioned above can, in principle, bond to the metal through one σ and two π bonds.

Metal oxides have frequently been employed to prepare imido complexes through reactions with primary amines (RNH_2) or isocyanates (RNCO) (eq. 1-2).⁴ We tried to prepare Mo-imido complexes by using molybdenum oxo complexes as precursors. Herein we report preparation and structure of $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}(\mu\text{-NPh})(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$, which has been formed from the reaction of $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$ with phenyl isocyanate.



Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for *ca.* 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for *ca.* 48 h, neutralized with K_2CO_3 , stirred over sodium metal, and distilled by

vacuum transfer. Toluene, diethyl ether, and tetrahydrofuran (THF) were stirred over sodium metal and distilled by vacuum transfer. Dichloromethane, dichloroethane, and aniline were stirred over CaH_2 and distilled by vacuum transfer. Isocyanates were used as received. NMR solvent (CDCl_3) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. *cis*- $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$, **1**, and $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$, **2**, were prepared by the literature method.¹⁵

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses were performed by the Korea Basic Science Center.

Preparation of $\text{MoOCl}_2(\text{S}_2\text{CNEt}_2)_2$, **3.** To 50 mL of dichloromethane containing 0.52 g (1.23 mmol) of *cis*- $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$, **1**, was added 0.32 mL (2.52 mmol) of neat chlorotrimethylsilane (Me_3SiCl). The resultant solution was refluxed for 2 h and filtered. The solvent was removed under vacuum to give yellow-brown solids. The resultant solids were washed with pentane (30 mL $\times$ 2), and then dried under vacuum to give 0.38 g (0.93 mmol, 76%) of $\text{MoOCl}_2(\text{S}_2\text{CNEt}_2)_2$, **3**. The product conveniently recrystallized from CH_2Cl_2 -pentane. ^1H NMR (CDCl_3): δ 3.87 (4H, m, diastereotopic CH_2CH_3), 3.76 (4H, m, diastereotopic CH_2CH_3), 1.35 (12H, t, $J=7.2$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 196.8 (CN), 44.0 (CH_2CH_3), 12.7 (CH_2CH_3). Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_5\text{Cl}_2\text{Mo}$: C, 25.06; H, 4.21; N, 5.84. Found: C, 24.86; H, 4.12; N, 5.79. Mp (decom.): 169–171 $^\circ\text{C}$. IR (KBr): 1537 (CN), 999 (CSS), 972 (CSS), 946 ($\text{Mo}=\text{O}$) cm^{-1} .

Preparation of $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}(\mu\text{-NPh})(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$, **4.** To 60 mL of toluene containing 0.42 g (1.03 mmol) of $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$, **2**, was added 0.39 mL (2.4 mmol)

of neat phenyl isocyanate (3.59 mmol). The resultant solution was refluxed for 24 h and filtered. The solvent was removed under vacuum to give yellow-brown solids. The resultant solids were washed with pentane (30 mL $\times$ 2), dried under vacuum, and recrystallized from THF-pentane to give a solid mixture, which consisted of red powders of **2** and yellow crystals of $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}\{\mu\text{-NPh}\}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$, **4**. The presence of these two species was confirmed by TLC (ethyl acetate/hexane), but several attempts to isolate **4** from the mixture product have not been successful. The yellow crystals of **4** were hand-picked. ^1H NMR (CDCl_3): δ 7.91–6.40 (25H, phenyl), 3.66 (4H, m, diastereotopic CH_2CH_3), 3.54 (4H, m, diastereotopic CH_2CH_3), 1.01 (12H, t, $J=7.1$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 203.3 (CN), 156.4 (CO), 129.3–125.5 (phenyl), 46.6 ($\text{CH}_2\text{-CH}_3$), 12.9 (CH_2CH_3). IR (KBr): 1712 (CO), 1478 (CN), 1025 (CSS), 998 (CSS) cm^{-1} .

X-ray Structure Determination. All X-ray data were collected with use of a Mac Science MXC diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 25 reflections in the range $20.0^\circ < 2\theta < 30.0^\circ$. Two 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. No absorption correction was applied. All calculations were carried out with use of the SHELXS-86¹⁶ and

SHELXL-93¹⁷ programs.

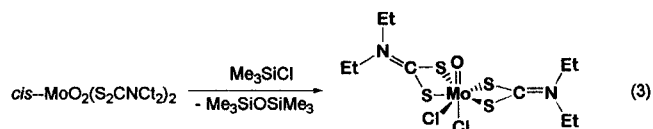
A yellow crystal of **3**, shaped as a block, of approximate dimensions $0.3 \times 0.4 \times 0.5 \text{ mm}^3$, was used for crystal and intensity data collection. The unit cell parameters and systematic absences $h0l$ ($l=2n+1$) and $0k0$ ($k=2n+1$) unambiguously indicated $P2_1/c$ as the space group. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations of F^2 s, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were generated in idealized positions and refined using a riding model.

A yellow crystal of **4**·THF, shaped as a block, of approximate dimensions $0.3 \times 0.4 \times 0.4 \text{ mm}^3$, was used for crystal and intensity data collection. The unit cell parameters and systematic absences $h00$ ($h=2n+1$), $0k0$ ($k=2n+1$), and $00l$ ($l=2n+1$) unambiguously indicated $P2_12_12_1$ as the space group. The structure was solved by the heavy atom method. The Mo and S atoms were refined anisotropically. The cocrystallized THF solvent (C61–C64, O2) exhibited a structural disorder and the best fit was obtained by considering these atoms to be distributed over two positions with the site occupation factors of 0.56:0.44 (C61–C64, O2: C61A–C64A, O2A). The hydrogen atoms bonded to the disordered tetrahydrofuran were not located. All the other hydrogen atoms were generated in idealized positions and refined using a riding model.

The selected bond distances and bond angles for **3** are shown in Table 2. Final atomic positional parameters for non-hydrogen atoms in **4** are shown in Table 3. The selected bond distances and bond angles for **4** are shown in Table 4.

Results and Discussion

Preparation. The dioxo Mo(VI) compound *cis*- $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$, **1**, reacts with Me_3SiCl in a refluxing dichloromethane to give $\text{MoOCl}_2(\text{S}_2\text{CNEt}_2)_2$, **3**, in moderate yield (eq. 3). Compound **3** was originally prepared from the reaction between **1** and HCl and its crystal structure was reported without detailed spectrometric data such as NMR and IR spectra.¹⁸ In ^1H NMR spectra, methylene protons (CH_2) show two multiplets at δ 3.87 and 3.76, due to their diastereotopic relationship.



The starting material **1** is known to react with PPh_3 to give a reduced Mo(IV) species, $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$, in a

Table 1. X-ray data collection and structure refinement for **3** and **4**

	3	4
formula	$\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_4\text{Cl}_2\text{Mo}$	$\text{C}_{45}\text{H}_{53}\text{N}_7\text{O}_7\text{S}_4\text{Mo}$
fw	479.36	1044.06
temperature, K	293	293
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
<i>a</i> , Å	8.908(1)	17.932(4)
<i>b</i> , Å	17.509(3)	22.715(5)
<i>c</i> , Å	12.683(2)	11.802(3)
β , deg	110.15(1)	
<i>V</i> , Å ³	1857.1(5)	4807(2)
<i>Z</i>	4	4
<i>d</i> _{calc} , g cm ⁻³	1.714	1.443
μ , mm ⁻¹	1.439	0.739
<i>F</i> (000)	968	2144
No. of reflections unique	3416	4148
No. of reflections with $I > 2\sigma(I)$	3108	4145
No. of parameters refined	181	210
2θ range (°)	3–50	3–50
scan type	ω -2 θ	ω -2 θ
scan speed	variable	variable
Max. Δ/σ	0.004	0.001
Max., in ($\Delta\rho$ (e Å ⁻³))	0.73	0.64
<i>GOF</i> (goodness-of-fit on F^2)	1.157	1.034
<i>R</i>	0.0611	0.0585
<i>wR</i> ₂ ^a	0.1385	0.1286

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

Table 2. Selected bond distances (Å) and bond angles (°) in **3**

Mo–O1	1.692(5)	Mo–Cl1	2.416(2)	Mo–Cl2	2.511(2)
Mo–S1	2.517(2)	Mo–S2	2.507(2)	Mo–S3	2.486(2)
Mo–S4	2.485(2)				
O1–Mo–Cl1	95.5(2)	O1–Mo–Cl2	175.9(2)	O1–Mo–S1	92.0(2)
O1–Mo–S2	92.4(2)	O1–Mo–S3	96.5(2)	O1–Mo–S4	96.7(2)
S1–Mo–S2	71.4(1)	S1–Mo–S3	139.2(1)	S1–Mo–S4	68.5(2)
S3–Mo–S4	148.6(2)				

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Mo1	10671(1)	-8583(1)	-1589(1)	40(1)
Mo2	9352(1)	-9053(1)	-1937(1)	42(1)
S1	-12018(2)	-8894(2)	-1826(3)	54(1)
S2	-11335(2)	-8476(1)	229(3)	55(1)
S3	-8842(2)	-10044(1)	-2515(3)	59(1)
S4	-8420(2)	-9384(2)	-534(3)	62(1)
O1	-10873(4)	-10110(3)	-2905(7)	54(2)
N1	-10335(5)	-9167(4)	-2974(8)	44(2)
N2	-9714(5)	-8512(4)	-657(7)	41(2)
N3	-10681(5)	-7914(4)	-2340(7)	46(2)
N4	-8860(5)	-8594(4)	-2830(8)	50(2)
N5	-10421(5)	-9583(4)	-1317(7)	43(2)
N6	-12627(6)	-9051(5)	209(10)	73(3)
N7	-7910(6)	-10467(5)	-922(9)	67(3)
C1	-12086(7)	-8824(6)	-397(11)	58(3)
C2	-12629(10)	-9075(8)	1529(15)	104(5)
C3	-12884(14)	-8571(11)	1919(23)	177(10)
C4	-13228(9)	-9486(8)	-343(16)	100(5)
C5	-13926(10)	-9164(9)	-410(17)	121(6)
C6	-8322(7)	-10021(6)	-1282(11)	58(3)
C7	-7544(8)	-10451(7)	165(13)	84(4)
C8	-7997(10)	-10630(8)	1101(15)	108(6)
C9	-7855(9)	-11028(7)	-1559(14)	90(5)
C10	7162(12)	-10987(11)	-2357(19)	152(9)
C60	-10592(6)	-9691(4)	-2426(8)	38(2)
C11	-10443(6)	-9100(5)	-4168(9)	47(3)
C12	-9872(2)	-9248(1)	-4912(2)	85(5)
C13	-9980(2)	-9206(1)	-6076(2)	101(5)
C14	-10664(2)	-9021(1)	-6501(2)	93(4)
C15	-11240(2)	-8878(1)	-5762(2)	98(5)
C16	-11132(2)	-8920(1)	-4599(2)	77(4)
C21	-9350(2)	-8194(1)	93(2)	57(3)
C22	-8709(2)	-7884(1)	-192(2)	86(5)
C23	-8350(2)	-7541(1)	618(2)	96(5)
C24	-8633(2)	-7510(1)	1713(2)	93(5)
C25	-9274(2)	-7820(1)	1998(2)	109(5)
C26	-9632(2)	-8163(1)	1188(2)	90(5)
C31	-10530(2)	-7432(1)	-2961(2)	47(3)
C32	-10105(2)	-6980(1)	-2498(2)	76(4)
C33	-9955(2)	-6479(1)	-3132(2)	83(4)
C34	-10229(2)	-6429(1)	-4230(2)	83(4)
C35	-10654(2)	-6881(1)	-4693(2)	103(5)
C36	-10804(2)	-7382(1)	-4059(2)	70(4)
C41	-8513(2)	-8162(1)	-3482(2)	44(3)
C42	-7782(2)	-8006(1)	-3232(2)	73(4)
C43	-7416(2)	-7589(1)	-3890(2)	91(5)
C44	-7782(2)	-7327(1)	-4798(2)	96(5)
C45	-8513(2)	-7483(1)	-5048(2)	100(5)
C46	-8879(2)	-7901(1)	-4390(2)	72(4)
C51	-10659(2)	-9954(1)	-423(2)	44(2)
C52	-11300(2)	-10296(1)	-499(2)	56(3)
C53	-11524(2)	-10636(1)	419(2)	75(4)
C54	-11107(2)	-10635(1)	1412(2)	81(4)
C55	-10466(2)	-10294(1)	1487(2)	67(4)
C56	-10242(2)	-9953(1)	569(2)	57(3)
O2	-8833(27)	-1411(23)	-6906(40)	226(17)
C61	-9224(33)	-1010(24)	-6417(43)	149(17)

Table 3. Continued

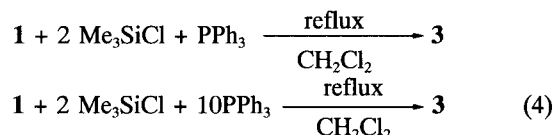
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
C62	-8767(34)	-986(29)	-5189(61)	168(21)
C63	-8536(35)	-1541(28)	-4916(52)	170(20)
C64	-8412(38)	-1758(30)	-5639(69)	203(27)
O2A	-8940(37)	-1893(25)	-6434(53)	219(21)
C61A	-8812(36)	-894(26)	6039(61)	125(17)
C62A	-9104(33)	-1227(28)	-4946(50)	132(20)
C63A	-9457(40)	-1516(36)	-6492(58)	168(23)
C64A	-9323(33)	-1810(24)	-5386(48)	139(17)

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

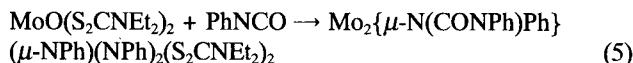
Table 4. Selected bond distances ($\text{\AA}$) and bond angles ($^\circ$) in **4**

Mo1-Mo2	2.628(1)	Mo1-S2	2.465(3)	Mo1-S1	2.532(3)
Mo2-S4	2.471(3)	Mo2-S3	2.525(3)	Mo1-N3	1.759(8)
Mo1-N2	2.046(8)	Mo1-N1	2.190(9)	Mo1-N5	2.338(9)
Mo2-N4	1.724(9)	Mo2-N2	2.053(8)	Mo2-N1	2.161(9)
Mo2-N5	2.380(8)	S1-C1	1.70(1)	S2-C1	1.73(1)
S3-C6	1.73(1)	S4-C6	1.70(1)	O1-C60	1.22(1)
N1-C11	1.43(1)	N1-C60	1.43(1)	N5-C60	1.37(1)
N2-C21	1.31(1)	N3-C31	1.34(1)	N4-C41	1.39(1)
N5-C51	1.42(1)	C1-N6	1.31(2)	C6-N7	1.32(2)
C11-N1-C60	119.3(9)	C11-N1-Mo2	131.0(7)	C60-N1-Mo2	96.1(6)
C11-N1-Mo1	129.3(7)	C60-N1-Mo1	94.5(6)	Mo2-N1-Mo1	73.3(3)
O1-C60-N5	132.7(9)	O1-C60-N1	125.1(9)	N5-C60-N1	102.2(8)
C60-N5-C51	122.6(8)	C31-N3-Mo1	167.3(7)	C41-N4-Mo2	172.5(7)
S2-Mo1-S1	70.3(1)	N3-Mo1-N2	102.2(4)	N3-Mo1-N1	98.6(4)
N2-Mo1-N1	102.6(3)	S4-Mo2-S3	70.4(1)	N4-Mo2-N2	104.4(4)
N4-Mo2-N1	98.2(4)	N2-Mo2-N1	103.4(3)	N3-Mo1-Mo2	106.3(3)
N2-Mo1-Mo2	50.2(2)	N1-Mo1-Mo2	52.3(2)	N5-Mo1-Mo2	56.9(2)
N4-Mo2-Mo1	108.1(3)	N2-Mo2-Mo1	50.0(2)	N1-Mo2-Mo1	53.4(2)
N5-Mo2-Mo1	55.41(2)				

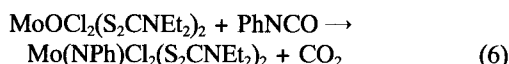
refluxing dichloroethane.¹⁹ In order to prepare $\text{MoCl}_2(\text{S}_2\text{-CNEt}_2)_2$, reactions between **1** and Me_3SiCl in the presence of PPh_3 , which is expected to act as an oxygen abstractor, have been carried out (eq. 4). In a refluxing dichloromethane, the stoichiometric reaction of **1** with Me_3SiCl and PPh_3 , in the mole ratio of $1:\text{Me}_3\text{SiCl}:\text{PPh}_3=1:2:1$, leads to the formation of **3**. The reaction of **1** with Me_3SiCl in the presence of excess PPh_3 (10-fold excess with respect to **1**) also gives **3**. These experimental results suggest that Me_3SiCl is superior to PPh_3 in abstracting oxide from the Mo metal in this reaction.



In order to prepare Mo-imido ($\text{Mo}=\text{NR}$; $\text{R}=\text{t-Bu, Ph}$) species, $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$, **2**, has been treated with the corresponding primary amines (RNH_2), but no reaction has occurred. The reaction of **2** with phenyl isocyanate ($\text{C}_6\text{H}_5\text{-NCO}$) gives an unusual product $\text{Mo}_2\{\mu\text{-N}(\text{CONPh})\text{Ph}\}\{\mu\text{-NPh}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2\}$, **4** (eq. 5). However, no reaction has occurred between **3** and *tert*-butyl isocyanate, butyl isocyanate, cyclohexyl isocyanate, or 2,6-diisopropylphenyl isocyanate.



Compound **4** is an Mo dimer that contains an Mo-Mo bond, two diethylthiocarbamato ligands, two terminal imido (NPh) ligands, and two bridging NPh ligands. In addition, the two equivalent Mo metals have been oxidized from a formal oxidation +4 to +5. As described below, the isocyanate oxygen (O1 in Figure 2) is not bonded to any atom in **4**, except for the isocyanate carbon atom. In addition, no bands assignable to N-H or O-H bonds are observed in the IR spectra of **4**. It is worth noting that $\text{MoOCl}_2(\text{S}_2\text{CNET}_2)_2$ reacted with PhNCO to give a monomeric species $\text{Mo}(\text{NPh})\text{Cl}_2(\text{S}_2\text{CNET}_2)_2$ (eq. 6).²⁰



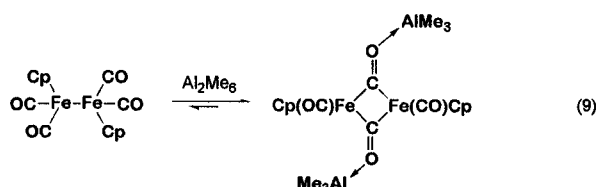
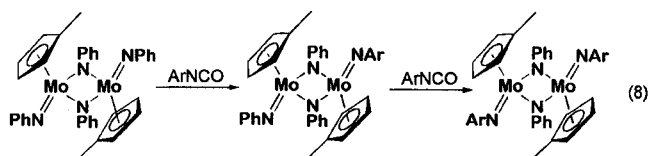
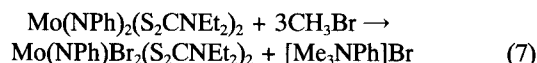
In ^1H NMR spectra of **4**, as in the complex **3**, methylene protons (CH_2) show two multiplets at δ 3.66 and 3.34, also due to their diastereotopic relationship. The presence of the CO group in **4** has been confirmed by IR (a band at 1712 cm^{-1}), $^{13}\text{C}\{^1\text{H}\}$ -NMR (a peak at δ 156.4), and X-ray crystallography (see below).

Three regions in IR spectra of dialkylthiocarbamato metal complexes are of considerable interest and have proven valuable in arguments concerning electronic and structural characteristics of these complexes.²¹ The $1450\text{--}1550\text{ cm}^{-1}$ region is attributed to the C-N vibration, $950\text{--}1050\text{ cm}^{-1}$ to the CSS vibration, and $300\text{--}400\text{ cm}^{-1}$ to the M-S vibration. In IR spectra of **4**, the band at 1478 cm^{-1} can be assigned as the C-N vibration in Et_2NCS_2 and the bands at 1025 and 998 cm^{-1} as the CSS vibrations.

Although we cannot give a clear-cut explanation for the formation of **4**, one possible mechanism is shown in Scheme 1. We have no evidence for the dimeric intermediate but it has probably undergone electrophilic attack of the phenyl isocyanate carbon at the bridging imido nitrogen atom to give the final product **4**.

Numerous reactions of imido complexes with electrophiles have been reported.¹ For instance, CH_3Br attacks the imido ligand in the related compound $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNET}_2)_2$ to remove the imido ligand completely from the metal (eq. 7).²² It has also been known that imido ligands react with such electrophiles as CO_2 , RNCO , or $\text{RN}=\text{C}=\text{NR}$ to form metallacycles by attack of the electrophilic carbon at the imido nitrogen atom.¹ However, the reaction of a different type has also been reported, in which the dimolybdenum

tetraimido complex $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{NPh})(\mu\text{-NPh})]_2$ reacts with excess para-tolyl isocyanate (NAr : $\text{Ar} = p\text{-tolyl}$) to give $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{NAr})(\mu\text{-NPh})]_2$, in a stepwise exchange of terminal imido ligands (eq. 8).²³ On the contrary to the metathesis of the terminal imido ligand with the isocyanate compound as shown in eq. 8, one of the bridging NPh ligands in **4** seemed to have been attacked by the electrophilic phenyl isocyanate carbon. The result suggests that bridging imido NPh ligand is more nucleophilic (or basic) than the terminal one and parallels the well known fact that a bridging CO is more basic at oxygen than a terminal CO (eq. 9).²⁴



Structure. Because X-ray crystallography is the only way to give a clear-cut evidence for the formation of **3**, some important crystallographic data such as an ORTEP drawing and the selected bond distances and bond angles are presented. Molecular structure of **3** with the atomic numbering scheme is shown in Figure 1. The coordination of the Mo metal can be described as a slightly distorted pentagonal bipyramid, with the oxygen (O1) and chlorine (Cl2) atoms occupying the axial sites. Compound **3** has two bidentate diethyldithiocarbamate groups, two *cis* Cl atoms, and one oxo group *trans* to the chloride ligand. The

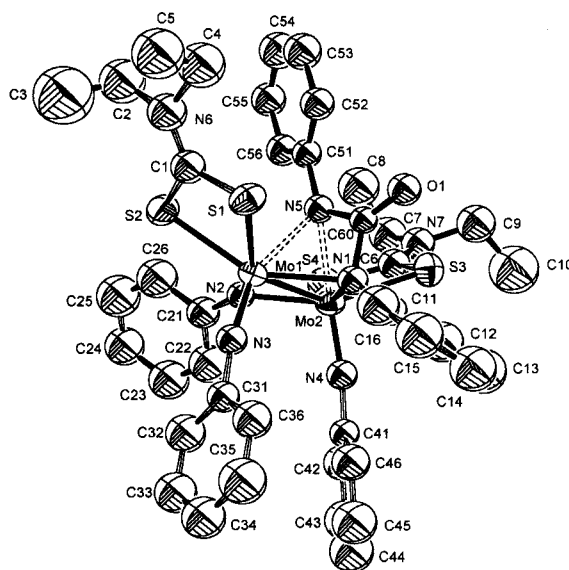
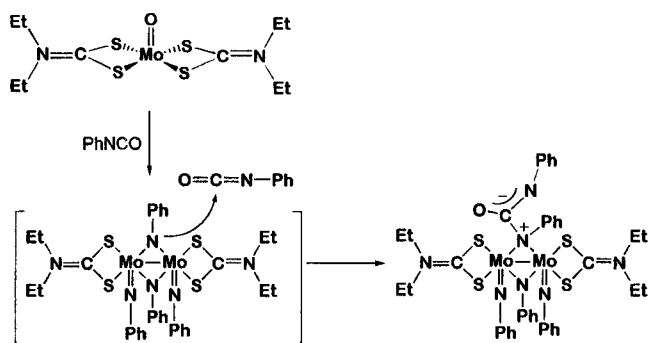


Figure 1. ORTEP drawing³³ of **4** showing the atom-labeling scheme and 50% probability thermal ellipsoids.



Scheme 1

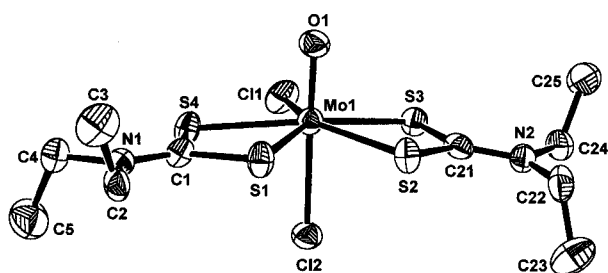


Figure 2. ORTEP drawing³³ of **3** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

equatorial plane, defined by S1, S2, S3, S4, and C11, is planar with the average atomic displacement of 0.051 Å. The Mo metal lies 0.204 Å above the equatorial plane.

Molecular structure of **4** with the atomic numbering scheme is shown in Figure 2, in which the disordered, cocrystallized THF molecule is omitted for clarity. Each Mo metal has an extremely distorted octahedral geometry, with a diethyldithiocarbamate ligand, a terminal NPh ligand, a bridging NPh ligand, and the other Mo moiety. Compound **4** has a dimeric structure bridged by the two NPh ligands, one of which is bonded to the phenyl isocyanate carbon atom. The molecular plane (or Mo₂N₂ core), defined by Mo1, Mo2, N1, and N2, is nearly planar with the average atomic displacement of 0.016 Å. The triangular planes defined by the Mo and two S atoms (Mo1, S1, S2 and Mo2, S3, S4) have dihedral angles of 35.5(2)–33.2(2)° with respect to the molecular plane.

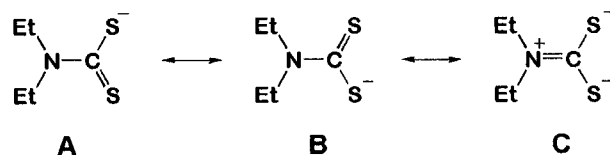
The distances of O1–Mo1 (3.818(8) Å), O1–Mo2 (3.909(8) Å), and O1–N1 (2.351(8) Å) indicate that there are no actual chemical bonds around the isocyanate oxygen (O1) except for O1–C60. The bond distances of C60–O1 and C60–N5 are 1.21(1) Å and 1.37(1) Å, respectively, indicating double bond characters for them. The bond distance of C60–N1 (1.43(1) Å) is consistent with the C–N single bond expected for C(sp²)-N(sp³, ArNR₂).²⁵ The sum of bond angles around C60 is very close to 360° (132.7°+125.1°+102.2°) that is expected for the sp²-carbon atom. Moreover, the plane defined by N1, N5, O1, and C60 is essentially planar with the average atomic displacement of 0.003 Å. These bonding parameters indicate that C60 is sp²-hybridized.

The Mo1–Mo2 bond distance of 2.628(1) Å is very close to the Mo–Mo distance (2.64 Å) in the Mo metal. The Mo–Mo distances in some related complexes are 2.645(1) Å in [(MeC₅H₄)₂Mo₂O₂(μ-O)(μ-NPh)],²⁶ 2.691(1) Å in [(MeC₅H₄)MoO(μ-NPh)]₂,²⁶ and 2.718(1) Å in [(MeC₅H₄)Mo(NPh)(μ-NPh)].²⁷

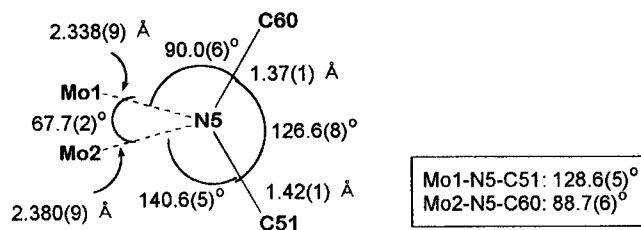
The Mo–N (terminal imido N) bond distance of 1.759(8) Å and 1.724(9) Å in **4** are consistent with those found for aryl imido ligands coordinated to molybdenum.^{1,28–30} The Mo–N–C bond angles of 167.3(7)° (C31–N3–Mo1) and 172.5(7)° (C41–N4–Mo2) are fairly typical of phenyl imido ligands in high oxidation state complexes, in which the metal is relatively electron-deficient and some π bonding between the imido nitrogen atom and the metal is likely.^{1,28,29} These angles, therefore, indicate that the imido group is linear and the Mo–N bond has a triple bond character with a sp-hybridized nitrogen. The Mo–N (bridging imido N) bond distance of 2.046(8)–2.190(9) Å in **4** indicate Mo–N single

bonds, because a metal–nitrogen single bond is expected to lie within 1.95–2.15 Å.³¹

The bonding parameters around the phenyl isocyanate nitrogen (N5) are somewhat interesting and they are shown below. The Mo–N (phenyl isocyanate nitrogen) distances of 2.338(9) Å (Mo1–N5) and 2.380(8) Å (Mo2–N5) are significantly longer than the sum (2.060 Å) of their covalent radii (Mo: 1.360, N: 0.700 Å), and therefore these are out of range from normal Mo–N single bonds.³¹ We are not sure whether elongated Mo–N bonds are extremely long Mo–N single bonds due to the steric congestion around the Mo metals or result from intramolecular van der Waals contacts (these distances are extremely shorter than the sum (2.95 Å) of the van der Waals radius of N (1.55 Å) and the metal radius of Mo (1.40 Å)). The Mo–C60 (phenyl isocyanate carbon) distances of 2.708(9) Å (Mo1–C60) and 2.716(11) Å (Mo2–C60) are also significantly shorter than the sum (3.10 Å) of van der Waals radius of C (1.70 Å) and the metal radius of Mo (1.40 Å), indicating van der Waals contacts. If the terminal NPh ligand is regarded as a six-electron donor, each Mo metal in **4** has 16 valence electrons without considering the two elongated Mo–N bonds (Mo1–N5 and Mo2–N5). On the other hand, if the terminal NPh ligand is regarded as a four-electron donor and if these two elongated Mo–N bonds are regarded as normal Mo–N single bonds, each Mo metal in **4** has 18 valence electrons.



The C–N bond distances in dialkyldithiocarbamate metal complexes have been reported to lie within the range of 1.313–1.334 Å, due to the contribution of the canonical form C among the resonance structures.³² The C–N bond distances in diethyldithiocarbamate ligand in **4** belong to this range. The N–C (N2–C21 vs. N1–C11) bond distances in the two bridging NPh ligands are significantly different from each other (1.31(1) vs. 1.43(1) Å). The longer bond of N1–C11 probably results from the electrophilic attack of the phenyl isocyanate carbon at the bridging imido nitrogen atom, which prevents the resonance between the nitrogen atom and the phenyl group to make the C–N bond shorter.



In summary, MoO(S₂CNEt₂)₂, **2**, reacted with phenyl isocyanate (PhNCO) to give an Mo dimer Mo₂{μ-N(CONPh)Ph}(μ-NPh)(NPh)₂(S₂CNEt₂)₂, **4**, which contains an Mo–Mo bond, two diethyldithiocarbamate ligands, two terminal imido (NPh) ligands, and two bridging imido (NPh) ligands. One of the two bridging NPh ligands seemed to have been attacked by the electrophilic phenyl isocyanate carbon, which suggests that the bridging imido NPh ligand is more

nucleophilic than the terminal one. However, **2** does not react with other isocyanates such as *tert*-butyl isocyanate, butyl isocyanate, cyclohexyl isocyanate, or 2,6-diisopropylphenyl isocyanate.

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