

Formation of $\text{Mo}(\text{NAr})(\text{PMe}_3)_2\text{Cl}_3$ and $\text{Mo}_2(\text{PMe}_3)_4\text{Cl}_4$ from Reduction of $\text{Mo}(\text{NAr})_2\text{Cl}_2(\text{DME})$ with Mg in the Presence of PMe_3 [Ar=2,6-diisopropylphenyl]

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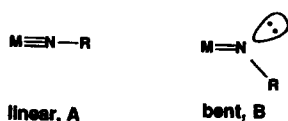
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Magnesium reduction of $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2\text{Cl}_2(\text{DME})$ in the presence of trimethylphosphine led to a mixture of $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **1**, and $\text{Mo}_2(\text{PMe}_3)_4\text{Cl}_4$, **2**. In solution **1** is slowly air-oxidized to $\text{Mo}(\text{N-2,6-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{OPMe}_3)(\text{PMe}_3)\text{Cl}_3$, **3**. **1** is chemically inert to carbon nucleophiles (ZnMe_2 , ZnEt_2 , AlMe_3 , AlEt_3 , LiCp , NaCp , TICp , NaCp^* , MeMgBr , EtMgBr), oxygen nucleophiles (LiOEt , $\text{LiO-}i\text{-Pr}$, LiOPh , LiOSPh), and hydrides (LiBEt_3H , LiBEt_3D). Crystal data for **1**: orthorhombic space group $P2_12_12_1$, $a=11.312(3)$ Å, $b=11.908(3)$ Å, $c=19.381(6)$ Å, $Z=4$, $R(wR_2)=0.0463$ (0.1067). Crystal data for **2**: monoclinic space group Cc , $a=18.384(3)$ Å, $b=9.181(2)$ Å, $c=19.118(3)$ Å, $\beta=124.98(1)^\circ$, $Z=4$, $R(wR_2)=0.0228$ (0.0568). Crystal data for **3**: orthorhombic space group $P2_12_12_1$, $a=11.464(1)$ Å, $b=14.081(2)$ Å, $c=16.614(3)$ Å, $Z=4$, $R(wR_2)=0.0394$ (0.0923).

Introduction

Since the first imido complexes, $\text{OsO}_3(\text{NR})$, were reported in 1959, transition-metal imido (or nitrene) complexes, $\text{L}_n\text{M}=\text{NR}$ (R: alkyl or aryl), have received continuous interest.¹ Although imido groups are usually considered to be chemically inert, some very reactive metal imido species have been reported to be involved, stoichiometrically or catalytically, in cycloaddition, transfer of a imido group, activation of C-H bonds, carbodiimide metathesis, and imine metathesis.² Two general types of imido complexes are now known, although Cundari's theoretical studies led to a conclusion that a minimum of eight resonance structures are required to describe the metal-imido linkage.³ The more common complexes of metals in a high oxidation state have a linear imido ligand with a metal-nitrogen triple bond character (**A**). In contrast, some zero-valent metals (Cr, W) possess a bent imido ligand with the lone pair on nitrogen (**B**).⁴ Bent imido species with formal M-N double bonds are more reactive than linear ones, because nucleophilic reactivity is enhanced in the bent NR ligand.⁵ We set out to prepare a bent imido complex by reducing a central metal, which is expected to make the nitrogen lone pair more free. As a bent imido precursor, $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2\text{Cl}_2(\text{DME})$ was chosen, which was recently prepared in high yield by Schrock and his coworkers.⁶

When $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2\text{Cl}_2(\text{DME})$ was treated with Mg powder in the presence of trimethylphosphine, unexpected products, *mer,trans*- $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **1**, and $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$, **2**, were obtained. In addition, compound **1** was gradually air-oxidized in solution to *mer,cis*- $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)(\text{OPMe}_3)(\text{PMe}_3)\text{Cl}_3$, **3**. Herein we report preparation, structure, and reactivity of these complexes.



Experimental Section

Unless otherwise stated, all the reactions were 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. Benzene, diethyl ether, and tetrahydrofuran (THF) were stirred over sodium metal and distilled by vacuum transfer. C_6D_6 was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. 2,6-Diisopropylaniline was distilled over CaH_2 and stored under argon. CO (99.9%) was purchased from Union Gas Co. and used as received. Sodium cyclopentadienylide (NaCp ; $\text{Cp}=\text{C}_5\text{H}_5$, 2 M in THF), thallium cyclopentadienylide (TlCp), sodium pentamethylcyclopentadienylide (NaCp^* ; $\text{Cp}^*=\text{C}_5(\text{CH}_3)_5$, 0.5 M in THF), sodium alkoxides (LiOR ; $\text{R}=\text{Et}$, *i*-Pr, Ph, SPh), lithium triethylborohydride (LiBEt_3H , 1 M in THF), lithium triethylborodeuteride (LiBEt_3D , 1 M in THF), trimethylphosphine (PMe_3 ; $\text{Me}=\text{CH}_3$, 1 M in toluene), magnesium powder, and 1,2-dimethoxyethane (DME) were purchased from Aldrich Co. and used as received. $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2\text{Cl}_2(\text{DME})$ was prepared by the literature method.⁶

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded with a Varian 200-MHz or a Bruker AMX-500 spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded with a Bruker AMX-500 spectrometer with reference to external 85% H_3PO_4 . IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Carbonylation reactions have been performed in a 60 mL of quartz pressure vessel (Kontes). Elemental analyses have been performed by Korea Basic Science Center.

Preparation of $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **1**

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Table 1. Crystallographic data and summary of data collection and structure refinement

	1	2	3
formula	C ₁₈ H ₃₅ NP ₂ Cl ₃ Mo	C ₁₂ H ₃₆ P ₄ Cl ₄ Mo ₂	C ₁₈ H ₃₅ NOP ₂ Cl ₃ Mo
fw	529.70	637.97	545.70
temperature, K	293	293	293
crystal system	orthorhombic	monoclinic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	Cc	P2 ₁ 2 ₁ 2 ₁
a, Å	11.312(3)	18.384(3)	11.464(1)
b, Å	11.908(3)	9.181(2)	14.081(2)
c, Å	19.381(6)	19.118(3)	16.614(3)
β, deg		124.98(1β)	
V, Å ³	2610(1)	2643.9(8)	2681.9(7)
Z	4	4	4
d _{calc} , g cm ⁻³	1.348	1.603	1.352
μ, cm ⁻¹			
F(000)	1092	1280	1124
n. of reflns used, I>2σ(I)	1871	2136	2191
no. of params	202	199	223
scan range	3<2θ<50	3<2θ<50	3<2θ<50
scan type	ω-2θ	ω-2θ	ω-2θ
Max. in Δρ (e Å ⁻³)	0.37	0.71	0.44
GOF on F ²	1.055	1.064	1.072
R	0.0463	0.0228	0.0394
wR ₂ ^a	0.1067	0.0568	0.0923

$$^a wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)]_2 / \Sigma [w(F_o^2)] \}^{1/2}$$

and Mo₂Cl₄(PMe₃)₄, **2**. Heating (20 h) 0.60 g (1 mmol) of Mo(N-C₆H₃-2,6-*i*-Pr₂)₂Cl₂(DME) with 2.6 mL (2.6 mmol) of PMe₃ (1 M in toluene) and 0.031 g (1.3 mmol) of magnesium powder in a refluxing THF (120 mL) gave a black brown solution. The resulting solution was filtered and then the solvent was removed under vacuum to give sticky brown stuff, which was extracted with pentane (30 mL × 2), and then the pentane was removed under vacuum to give violet solids. These solids recrystallized from diethylether to give blue crystals of Mo₂Cl₄(PMe₃)₄, **2**, (0.10 g, 0.16 mmol, 16%). The remaining orange solids after pentane extraction were dried under vacuum to give 0.20 g (0.38 mmol, 38%) of Mo(N-C₆H₃-2,6-*i*-Pr₂)(PMe₃)₂Cl₃, **1**, which conveniently recrystallized from toluene/octane.

Compound **1**. ¹H NMR (C₆D₆): δ 2.12 (sept, 2H, CHMe₂), 1.26 (m, 12H, CHMe₂), 0.87 (t, 18H, J_{P-H}=7.1 Hz, PMe₃). ¹³C{¹H}-NMR (C₆D₆): δ 34.38 (CHMe₂), 22.67 (CHMe₂), 14.23 (PMe₃). ³¹P{¹H}-NMR (C₆D₆): δ 27.87 (s). Anal. Calcd for C₁₈H₃₅NP₂Cl₃Mo: C, 40.81; H, 6.66; N, 2.64. Found: C, 41.38; H, 7.23; N, 2.48. mp: 200-202 °C. IR (KBr): 2962, 2912, 2869, 1588, 1460, 1415, 1307, 1287, 1128, 1057, 955 cm⁻¹.

Compound **2**. ¹H NMR (C₆D₆): δ 1.52 (t, J_{P-H}=4.5 Hz, PMe₃). ¹³C{¹H}-NMR (C₆D₆): δ 12.60 (PMe₃). IR (KBr): 2962, 2912, 2869, 1588, 1460, 1415, 1307, 1287, 1128, 1057, 955 cm⁻¹.

Formation of Mo(N-2,6-*i*-Pr₂-C₆H₃)(OPMe₃)(PMe₃)Cl₃, **3.** When the solution of toluene/octane containing **1** was allowed to be in contact with air for 72 h, **1** was slowly oxidized to *mer,cis*-Mo(N-C₆H₃-2,6-*i*-Pr₂)(OPMe₃)(PMe₃)Cl₃, **3**.

Compound **3**. ¹H-NMR (C₆D₆): δ 2.12 (sept, 2H, CHMe₂), 1.47 (d, 9H, J_{P-H}=6.85 Hz, OPMe₃), 1.04 (d, 12H, J=12.60 Hz, CHMe₂), 0.88 (d, 9H, J_{P-H}=6.90 Hz, PMe₃). IR (KBr): 2967, 2924, 2868, 1460, 1419, 1307, 1292, 1170, 1129, 1058, 989, 952, 865, 802, 757 cm⁻¹.

X-ray Structure Determination. All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with 20<2θ<30°. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored every 1 h during data collection. Data were corrected for Lorentz and polarization effects. Decay corrections were made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out on the personal computer with use of the SHELXS-86⁷ and SHELXL-93⁸ programs.

A red crystal of **1**, shaped as a plate, of approximate dimensions 0.1×0.3×0.4 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 (*h*=2*n*+1), 0*k*0 (*k*=2*n*+1), 00*l* (*l*=2*n*+1), unambiguously indicated P2₁2₁2₁ as a space group. The structure was solved by the heavy atom methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model.

A blue crystal of **2**, shaped as a block, of approximate dimensions 0.3×0.4×0.4 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *hkl* (*h*+*k*=2*n*+1), *h*0*l* (*h*, *l*=2*n*+1), 0*kl* (*k*=2*n*+1), *hk*0 (*h*+*k*=2*n*+1), *h*00 (*h*=2*n*+1), 0*k*0 (*k*=2*n*+1), 00*l* (*l*=2*n*+1), indicated two possible space groups: *Cc* and *C2/c*. A statistical analysis of intensities suggested a non-centrosymmetric space group, and the structure converged only in *Cc*. The structure was solved by the direct methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model.

A light green-yellow crystal of **3**, shaped as a block, of approximate dimensions 0.2×0.4×0.5 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 (*h*=2*n*+1), 0*k*0 (*k*=2*n*+1), 00*l* (*l*=2*n*+1), unambiguously indicated P2₁2₁2₁ as a space group. The structure was solved by the heavy atom methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model.

Final atomic positional parameters for **1** and **3** are shown in Tables 2 and 3, respectively. The selected bond distances and bond angles are shown in Tables 4 and 5; final atomic positional parameters for nonhydrogen atoms for **2**, anisotropic thermal parameters, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and calculated structure factors are available as supplementary material.

Results and Discussion

Preparation. Treatment of Mo(N-C₆H₃-2,6-*i*-Pr₂)₂

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for **1**

	x	y	z	U (eq) ^a
Mo	1534(1)	9390(1)	8761(1)	45(1)
CL1	458(3)	7561(2)	8750(2)	80(1)
CL2	2584(3)	8583(3)	7811(2)	77(1)
CL3	219(3)	9763(3)	9691(2)	98(1)
P1	-91(4)	10074(3)	7962(2)	88(1)
P2	2962(3)	8368(3)	9547(2)	75(1)
N	2271(5)	10680(5)	8781(4)	45(2)
C1	-276(20)	11609(15)	8045(10)	155(4)
C2	-1504(16)	9519(15)	8080(10)	155(4)
C3	177(18)	9884(15)	7060(9)	155(4)
C4	4386(19)	8908(27)	9509(14)	222(8)
C5	3194(21)	6962(24)	9293(13)	222(8)
C6	2523(19)	8095(25)	10383(13)	222(8)
C7	2840(7)	11728(7)	8801(6)	51(2)
C8	3715(8)	11942(9)	8303(6)	59(3)
C9	4265(11)	13001(10)	8324(6)	76(3)
C10	3934(11)	13785(9)	8782(7)	82(3)
C11	3104(12)	13553(10)	9258(7)	87(4)
C12	2513(9)	12543(8)	9289(5)	57(3)
C13	4122(10)	11080(10)	7779(6)	68(3)
C14	5446(12)	10843(12)	7843(8)	105(5)
C15	3715(17)	11402(18)	7060(8)	147(7)
C16	1622(11)	12306(10)	9850(7)	81(3)
C17	738(13)	13253(14)	9935(9)	122(6)
C18	2258(15)	12144(20)	10521(9)	149(8)

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

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

	x	y	z	U (eq) ^a
Mo	-1598(1)	-9456(1)	-8788(1)	48(1)
CL1	-1403(2)	-9004(2)	-10199(1)	76(1)
CL2	-2716(2)	-10828(2)	-9171(1)	79(1)
CL3	-918(2)	-7935(1)	-8338(1)	75(1)
P1	-2275(2)	-9891(2)	-7391(1)	59(1)
P2	-4070(2)	-8048(2)	-9155(1)	66(1)
O	-3245(4)	-8747(4)	-8803(4)	78(2)
N	-276(5)	-10013(4)	-8688(3)	52(1)
C1	-1696(9)	-11013(7)	-7083(6)	95(3)
C2	-3860(8)	-10048(9)	-7332(6)	101(4)
C3	-1954(11)	-9067(8)	-6596(5)	110(4)
C4	-3428(13)	-7132(9)	-9707(8)	142(3)
C5	-5058(13)	-8596(10)	-9807(9)	142(3)
C6	-4857(13)	-7534(10)	-8391(8)	142(3)
C7	836(6)	-10413(5)	-8677(5)	62(2)
C8	1662(8)	-10138(6)	-8078(6)	80(2)
C9	2771(10)	-10520(10)	-8154(9)	130(4)
C10	3061(9)	-11120(12)	-8719(10)	159(6)
C11	2279(10)	-11377(10)	-9311(9)	137(5)
C12	1139(7)	-11079(7)	-9278(6)	79(2)
C13	1324(8)	-9472(7)	-7406(6)	84(2)
C14	1507(11)	-9937(8)	-6572(7)	113(4)
C15	2016(12)	-8569(7)	-7450(8)	119(4)
C16	262(9)	-11436(7)	-9871(5)	82(3)
C17	659(12)	-11463(10)	-10725(6)	134(5)
C18	-94(13)	-12434(10)	-9629(8)	131(4)

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

Table 4. Selected bond distances (\AA) and bond angles (deg) for **1** and **3**

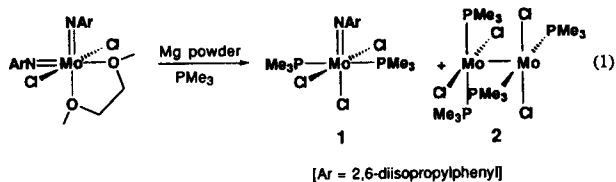
	1	3
Bond Distances		
Mo-N	1.748(6)	1.715(5)
Mo-CL1	2.495(3)	2.439(2)
Mo-CL2	2.393(3)	2.404(2)
Mo-CL3	2.378(3)	2.439(2)
Mo-P1	2.538(3)	2.524(2)
Mo-P2	2.531(3)	
Mo-O		2.137(4)
N-C7	1.405(10)	1.394(9)
P2-O		1.485(5)
Bond Angles		
Mo-N-C7	178.7(6)	174.0(5)
N-Mo-CL1	179.0(3)	97.6(2)
N-Mo-CL2	97.6(3)	97.4(2)
N-Mo-CL3	96.8(3)	95.2(2)
N-Mo-P1	94.4(2)	94.1(2)
N-Mo-P2	96.0(2)	
N-Mo-O		175.0(2)
P1-Mo-P2	169.59(12)	
P1-Mo-O		81.5(2)
Mo-O-P2		151.3(3)
CL2-Mo-CL3	165.59(11)	166.69(8)

Table 5. Selected bond distances (\AA) and bond angles (deg) for **2**

Bond Distances			
Mo1-Cl1	2.425(4)	Mo2-Cl3	2.430(3)
Mo1-Cl2	2.406(4)	Mo2-Cl4	2.398(4)
Mo1-P1	2.539(4)	Mo2-P3	2.555(4)
Mo1-P2	2.545(4)	Mo2-P4	2.537(4)
Mo1-Mo2	2.1310(6)		
Bond Angles			
Cl2-Mo1-Cl1	135.89(5)	Cl4-Mo2-Cl3	135.24(4)
Cl1-Mo1-P1	84.75(13)	Cl3-Mo2-P3	84.88(12)
Cl1-Mo1-P2	84.72(14)	Cl3-Mo2-P4	85.50(14)
Cl2-Mo1-P2	86.08(13)	Cl4-Mo2-P4	85.7(2)
Cl2-Mo1-P1	85.87(14)	Cl4-Mo2-P3	85.4(2)
P1-Mo1-P2	155.06(4)	P4-Mo2-P3	155.56(4)
Mo2-Mo1-Cl1	112.92(12)	Mo1-Mo2-Cl3	112.69(11)
Mo2-Mo1-Cl2	111.19(12)	Mo1-Mo2-Cl4	112.07(12)
Mo2-Mo1-P1	101.80(11)	Mo1-Mo2-P3	102.25(10)
Mo2-Mo1-P2	103.13(12)	Mo1-Mo2-P4	102.20(11)

Cl₂(DME) with Mg powder in the presence of PMe₃ in a refluxing tetrahydrofuran gives *mer,trans*-Mo(N-C₆H₅-2,6-*i*-Pr₂)(PMe₃)₂Cl₃, **1** and Mo₂Cl₄(PMe₃)₄, **2** (eq 1). The Mo metal has been formally reduced from Mo(VI) to Mo(V) in **1** and to Mo(II) in **2**. It is worth noting that the strongly bound ligands, the linear imido and the chelating DME groups, have been replaced during the reaction. Unfortunately, we can not give an explanation for this reduction. **2** was originally prepared from the reaction of K₄Mo₂Cl₈ with excess PMe₃ in ethanol and structurally characterized.⁹ Since the two Mo metals in **2** have a formal oxidation state of +2 (d⁴) and the ligands are placed in an eclipsed configuration, the

Mo-Mo bond is a quadruple bond with the electronic configuration of $\sigma^2\pi^4\delta^2$. Because an X-ray crystallography is the only way to give an evidence for the formation of **2**, some important data of an X-ray crystal structure such as an ORTEP drawing and the selected bond distances and bond angles are presented (*vide infra*).



In ^1H NMR spectra, methyl protons of PMe_3 in **1** exhibit a triplet at δ 0.87 ($J_{\text{P-H}}=7.1$ Hz), because of the virtual coupling by which methyl protons appear to be coupled both to its own and to the *trans*-phosphorus nucleus about equally.¹⁰ The *trans* orientation of two phosphine ligands is confirmed by X-ray crystallography (*vide infra*). In $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra, compound **1** shows a singlet for PMe_3 at δ 27.87.

Structure. Molecular structures of **1**, **2**, and **3** with the atomic numbering schemes are shown in Figures 1-3, respectively.

In compound **1**, the coordination sphere of the Mo metal can be described as a distorted octahedron. **1** has an NAr group, three *mer*-Cl atoms, and two *trans*-phosphine ligands. The equatorial plane, defined by Mo, P1, P2, Cl1, and N1, is essentially planar with the average displacement of 0.012 Å from this plane. The bond distance of (2.495(3) Å) of Mo-Cl, *trans* to the NAr group, is significantly longer than those of the other two Mo-Cl bonds (2.393(3) Å and 2.378(3) Å), probably due to a higher *trans*-influencing effect of the imido ligand (NAr).^{1c}

In compound **2**, the coordination sphere of each Mo metal can be described as a square pyramid. **2** is an Mo dimer with an Mo-Mo quadruple bond, in which all the ligands are in an eclipsed configuration.

In compound **3**, the coordination sphere of the Mo metal

can be described as a distorted octahedron. **3** has an NAr group, three *mer*-Cl atoms, one phosphine, and one phosphine oxide. The PMe_3 and O=PMe_3 ligands are mutually *cis*. The Mo metal lies 0.259(1) Å above the equatorial plane, defined by Cl1, Cl2, Cl3, and P1 atoms, on which the four atoms are coplanar with the average displacement of 0.009 Å.

Of particular interest are the bonding parameters of the Mo-N-C bonds. The Mo-N-C bond angles of $178.7(6)^\circ$ in **1** and $174.0(5)^\circ$ in **3** are fairly typical of diisopropylphenyl 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.^{1c,11} 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 bond distances of 1.748(6)^o in **1** and 1.715(5)^o in **3** are also consistent with those found for aryl imido ligands coordinated to molybdenum.^{1c,11,12} The Mo-P bond distances in the three complexes (2.524-2.555 Å) are within the values (2.497-2.546 Å) of known compounds.¹³

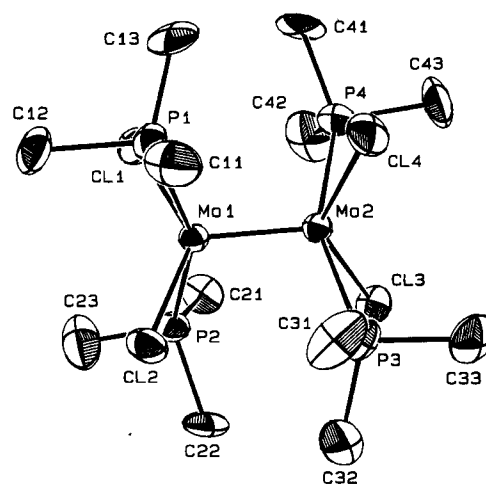


Figure 2. ORTEP drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

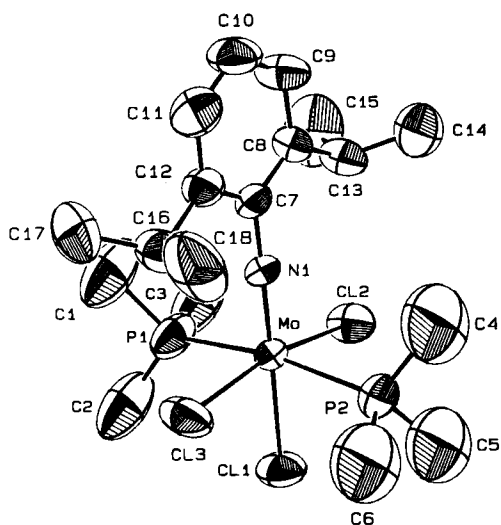


Figure 1. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

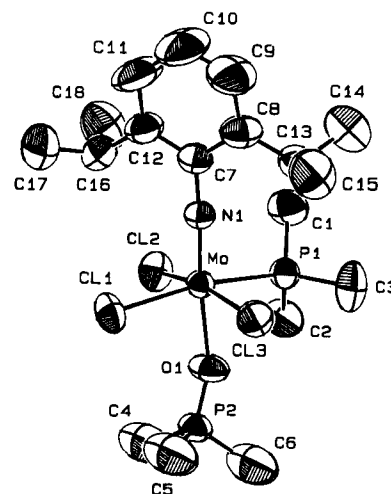
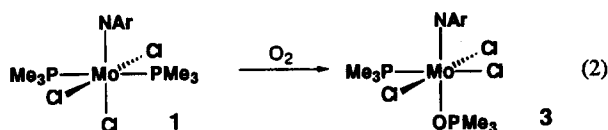


Figure 3. ORTEP drawing of **3** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Reactivity of 1. Compound **1** is gradually air-oxidized to *mer,cis*- $\text{Mo}(\text{N-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)(\text{OPMe}_3)(\text{PMe}_3)\text{Cl}_3$, **3**, when the recrystallization of **2** was attempted from toluene-octane (eq 2). It is interesting to note that only one of the both PMe_3 ligands been converted into the corresponding phosphine oxide, $\text{O}=\text{PMe}_3$, and the mutual orientation of the phosphines has also been changed from *trans* to *cis*. Because **1** is a saturated, 18-electron complex, this reaction is likely to involve a dissociative fashion. In addition the intermediate, formed by PMe_3 dissociation, seems to be in pseudorotation, considering the change in the mutual orientation of two phosphine groups during the reaction. An alternative pathway, which involves a chloride dissociation followed by oxidation of the coordinated PMe_3 , cannot be ruled out.



Any sign of reaction has not been observed in the reactions of **1** with mild alkylating reagents such as ZnMe_2 , ZnEt_2 , AlMe_3 , and AlEt_3 . **1** does not react with strong carbon nucleophiles, such as LiCp , NaCp , TiCp , NaCp^* ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}^* = \text{C}_5\text{Me}_5$), and Grignard reagents (MeMgBr , EtMgBr), even under vigorous conditions (in refluxing toluene) at all. **1** is also inert toward oxygen nucleophiles such as lithium alkoxides (LiOR ; $\text{R} = \text{Et}$, *i*-Pr, Ph, SPh) and toward hydrides (LiBEt_3H , LiBEt_3D).

Recently, Bergman and his co-workers reported an insertion of CO into an $\text{Ir} \equiv \text{N}$ bond in $\text{Cp}^*\text{Ir}(\equiv \text{N}^t\text{Bu})$, ($\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$), which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.¹⁴ The results of above studies prompted us to investigate the possibility of insertion of CO into Mo-imido bonds in our compounds. However, no reactions of compound **1** with CO (up to 2 atm) have been observed.

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Supplementary Material Available. Tables of atomic coordinates for **2**, bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atom (13 pages); listings of observed and calculated structure factors (14 pages).

References

- (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.

- (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, U.S.A., 1988.
- (d) Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. Vol. 2, Pergman Press: Oxford, England, 1987; pp 161-188. (e) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (f) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *8*, 279.
- Morrison, D. L.; Wigley, D. E. *Inorg. Chem.* **1995**, *34*, 2610 and references therein.
- Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879.
- (a) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (b) Massey, S. T.; Mansour, B.; McElwee-White, L. *J. Organomet. Chem.* **1995**, *485*, 123.
- (a) Saravanamuthu, A.; Ho, D. M.; Kerr, M. E.; Fitzgerald, C.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1993**, *32*, 2202. (b) Bradley, D. C.; Hodge, S. R.; Runnacles, J. D.; Hughes, M.; Mason, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1663. (c) Minelli, M.; Carson, M. R.; Whisenhunt, D. W.; Imhof, W.; Huttner, G. *Inorg. Chem.* **1990**, *29*, 4801. (d) Sloan, O. D.; Thornton, P. *Polyhedron* **1988**, *7*, 329. (e) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157. (f) Nugent, W. A.; Harlow, R. L.; McKinney, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 7265. (g) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
- Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *31*, 2287.
- Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
- Sheldrick, G. M. *SHELXL-93*, University of Gottingen, 1993.
- Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.
- Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons: 2nd ed., New York, U. S. A. 1994; p 237.
- (a) Bazan, G. C.; Schrock, R. R.; O'Regen, M. B. *Organometallics* **1991**, *10*, 1062. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158.
- Bell, A.; Clegg, W.; Dyer, P. W.; Elsegood, M. R. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2247.
- Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.
- Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.