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Syntheses and X-ray Crystal Structures of Dichlorobis(tert-butylimido) Complexes of Molybdenum(VI); Potential Precursors to Molybdenum Nitride and Molybdenum Carbonitride

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The bistertbutylimido complexes $[MoCl(\mu\text{-}Cl)(NBu^t)_2(NH_2Bu^t)]_2$, **1**, and $MoCl_2(NBu^t)_2(py)_2$, **2** (py = pyridine), were prepared by reacting $MoCl_2(NBu^t)_2(dme)$ (dme = dimethoxyethane) with excess Bu^tNH_2 and pyridine, respectively. Their structures were determined by X-ray crystallography. **1** has a pseudo edge-shared bioctahedral geometry with two Cl ligands bridging the Mo centers unequally. Pertinent bond distances and angles for **1**, Mo = NBu^t_{bent} = 1.737(3) Å, ∠Mo = N-CMe_3 = 154.0(2)°; Mo = NBu^t_{linear} = 1.725(3) Å, ∠Mo = N-CMe_3 = 172.4(2)°; Mo-Bu^tNH_2 = 2.233(2) Å; Mo-$Cl_{bridging}$ = 2.575(1) and 2.835(1) Å, and Mo-$Cl_{terminal}$ = 2.428(1) Å. Crystal data for **1**: triclinic, space group $P\bar{1}$, a = 8.897(4) Å, b = 10.518(3) Å, c = 10.663(3) Å, α = 107.68(2)°, β = 98.03(3)°, γ = 99.26(3)°, V = 919.3(5) Å^3, Z = 1, D_c = 1.381 g/mL. **2** is mononuclear with a distorted octahedral geometry with two *trans* Cl ligands, two *cis*-oriented Bu^tN = ligands, and two py ligands *trans* to the imido groups. Pertinent averaged bond distances and angles for **2**, Mo = NBu^t_{bent} = 1.736(4) Å, ∠Mo = N-CMe_3 = 163.8(4)°; Mo = NBu^t_{linear} = 1.705(5) Å, ∠Mo = N-CMe_3 = 173.4(4)°; Mo-N(py) = 2.44(1), Mo-Cl = 2.421(3) Å. Crystal data for **2**: orthorhombic, space group $Pna2_1$, a = 16.860(2) Å, b = 8.920(3) Å, c = 15.120(3) Å, V = 2274.1(9) Å^3, Z = 4, D_c = 1.362 g/mL. A potential application of **2** as a single-source precursor to grow molybdenum nitride and molybdenum carbonitride thin films by low pressure chemical vapor deposition (LPCVD) was explored. Cubic phase thin films ($a_{thin\ film}$ = 4.16 - 4.20 Å) were grown at temperatures between 450 °C and 650 °C with hydrogen as carrier gas. At 450 °C, thin films of molybdenum nitride were obtained. With temperature of deposition increased from 450 °C to 650 °C, the ratio C/Mo increased from 0.03 to 0.5 whereas the ratio N/Mo decreased from 0.7 to 0.3. Thus, thin films of molybdenum carbonitride were deposited at 650 °C.

INTRODUCTION

Organoimido ligands, =NR, stabilize complexes of early transition metals in high oxidation states through multiply bonded metal-nitrogen linkages.[1] Among many reactions involving these complexes, their use in homogeneous catalysis, such as olefin metathesis, was explored.[2] These organoimido complexes as precursors to grow metal nitride and carbonitride thin films by CVD (chemical vapor deposition) are under intensive investigation.[3] Here, we report the syntheses and characterization of two dichlorobis(tert-butylimido) molybdenum complexes, $[MoCl(\mu\text{-}Cl)(NBu^t)_2(NH_2Bu^t)]_2$, **1**, and $MoCl_2(NBu^t)_2(py)_2$, **2** (py = pyridine). Employing **2** as a potential single-source precursor to grow molybdenum nitride and carbonitride thin films by CVD was explored.

RESULTS AND DISCUSSION

Characterization

Simple ligand displacement reactions of $MoCl_2(NBu^t)_2(dme)$ (dimethoxyethane) with excess Bu^tNH_2 and pyridine in hexane generate air-sensitive orange solids **1** and **2**, respectively, in good yields.

Crystals of satisfactory quality of **1** and **2** were precipitated from toluene solutions at -15 °C. The molecular structures of **1** and **2**, determined by X-ray diffraction, are shown in Figs. 1 and 2. Atomic parameters of **1** and **2** are shown in Tables 1 and 2, respectively. Bond distances and bond angles of **1** and **2** are listed in Tables 3 and 4, respectively. NMR data of **1** and **2** in solution are consistent with the diffraction results.

1 has a pseudo edge-shared bioctahedral geometry

Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

with bridging chloro Cl(1) and Cl(1′), and terminal chloro Cl(2), amino N(1), and imido N(2) and N(3) ligands coordinated to the Mo atoms. The overall geometry is closely related to the structure of $[WCl(\mu\text{-}Cl)(NBu^t)_2(NH_2Bu^t)]_2$.[4] One imido group of **1** is almost linear and has a short bond (Mo-N(3)-C(9) = 172.4(2)°, Mo-N(3) = 1.725(3) Å), whereas the other is more angular with a longer bond (Mo-N(2)-C(5) = 154.0(2)°, Mo-N(2) = 1.737(3) Å). Hence the Mo-N(3) linkage has more metal-nitrogen triple-bond character than the Mo-N(2) linkage. A similar arrangement of imido ligands is observed for other bisimido complexes of molybdenum, such as $Mo(NPh)_2(S_2CNEt_2)_2$ and $Mo(NAr)_2(NHAr)_2$ (Ar = 2,6-diisopropylphenyl).[5,6] The bridging chlorides connect unsymmetrically between the molybdenum atoms (Mo-Cl(1) = 2.575(1) Å, Mo-Cl(1′) = 2.835(1) Å). The long Mo-Cl(1′) bond is probably caused by the linear imido ligand *trans* to it, which has a better π-donating ability than the bent one. A similar *trans*-influence is observed for $[WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)]_2$ and $[WCl_3(\mu\text{-}Cl)(NPr^i)]_2$ (Ph = phenyl, Pr^i = isopropyl).[7,8]

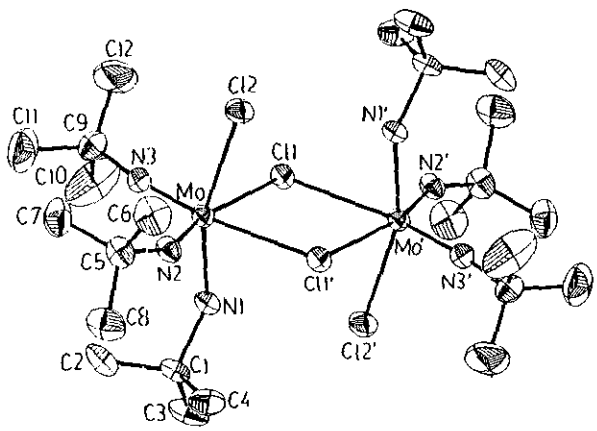


Fig. 1. Molecular structure of **1**, $[MoCl(\mu\text{-}Cl)(NBu^t)_2(NH_2Bu^t)]_2$.

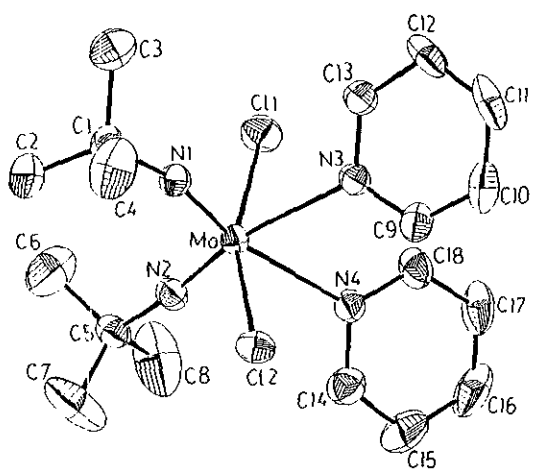


Fig. 2. Molecular structure of **2**, $MoCl_2(NBu^t)_2(py)_2$.

Table 1. Atomic Coordinates and Isotropic Thermal Parameters of **1**

	x	y	z	Beq
Mo	0.90445(3)	0.81193(3)	0.33623(3)	2.993(10)
Cl1	1.06480(8)	0.90060(7)	0.57789(7)	3.31(3)
Cl2	1.15007(9)	0.85986(9)	0.26703(9)	4.49(4)
N1	0.7161(3)	0.85666(23)	0.45041(24)	3.16(11)
N2	0.9047(3)	0.64234(24)	0.31879(25)	3.58(12)
N3	0.7942(3)	0.8125(3)	0.18990(24)	3.68(12)
C1	0.5970(3)	0.7548(3)	0.4789(3)	3.87(15)
C2	0.5084(4)	0.6514(4)	0.3460(4)	5.57(20)
C3	0.4872(4)	0.8337(4)	0.5520(5)	5.99(23)
C4	0.6841(4)	0.6909(4)	0.5668(4)	5.39(21)
C5	0.8956(4)	0.4992(3)	0.2417(3)	4.41(16)
C6	1.0637(5)	0.4834(4)	0.2490(5)	6.81(24)
C7	0.8161(5)	0.4670(4)	0.0980(4)	6.51(22)
C8	0.8078(6)	0.4069(4)	0.3051(5)	6.9(3)
C9	0.7094(4)	0.8324(4)	0.0734(3)	4.87(17)
C10	0.5818(8)	0.9018(8)	0.1187(6)	11.6(5)
C11	0.6360(6)	0.6965(6)	-0.0351(5)	8.7(3)
C12	0.8203(8)	0.9176(8)	0.0263(6)	13.4(5)
HN1A	0.772	0.911	0.541	3.8
HN1B	0.657	0.896	0.396	3.8
H2A	0.580	0.602	0.302	6.1
H2B	0.462	0.694	0.292	6.1
H2C	0.436	0.591	0.371	6.1
H3A	0.393	0.778	0.555	6.2
H3B	0.459	0.902	0.514	6.2
H3C	0.546	0.880	0.642	6.2
H4A	0.758	0.647	0.522	6.0
H4B	0.614	0.623	0.585	6.0
H4C	0.734	0.764	0.645	6.0
H6A	1.075	0.390	0.213	7.8
H6B	1.128	0.524	0.336	7.8
H6C	1.103	0.532	0.190	7.8
H7A	0.713	0.478	0.087	6.8
H7B	0.818	0.375	0.043	6.8
H7C	0.881	0.531	0.066	6.8
H8A	0.798	0.313	0.261	6.8
H8B	0.709	0.426	0.319	6.8
H8C	0.875	0.433	0.396	6.8
H10A	0.543	0.952	0.060	10.5
H10B	0.601	0.961	0.208	10.5
H10C	0.495	0.827	0.106	10.5
H11A	0.572	0.704	-0.111	8.6
H11B	0.578	0.632	-0.004	8.6
H11C	0.725	0.661	-0.065	8.6
H12A	0.890	0.994	0.094	10.9
H12B	0.779	0.947	-0.045	10.9
H12C	0.887	0.855	-0.012	10.9

2 is a mononuclear complex with a distorted octahedral geometry about the molybdenum center with two *trans* chloro ligands, two *cis*-oriented tertbutylimido ligands, and

Table 2. Bond Distances and Bond Angles of **1**

Bond Distance (Å)			
Mo-Cl(1)	2.5750(13)	C(1)-C(2)	1.513(5)
Mo-Cl(1′)	2.8350(12)	C(1)-C(3)	1.527(5)
Mo-Cl(2)	2.4281(13)	C(1)-C(4)	1.509(5)
Mo-N(1)	2.2330(24)	C(5)-C(6)	1.525(5)
Mo-N(2)	1.7366(25)	C(5)-C(7)	1.506(5)
Mo-N(3)	1.7253(25)	C(5)-C(8)	1.520(5)
		C(9)-C(10)	1.503(6)
N(1)-C(1)	1.512(3)	C(9)-C(11)	1.513(6)
N(2)-C(5)	1.462(4)	C(9)-C(12)	1.469(6)
N(3)-C(9)	1.450(4)		
Bond Angle (°)			
Cl(1)-Mo-Cl(1′)	74.69(4)	N(1)-C(1)-C(2)	108.1(3)
Cl(1′)-Mo-Cl(2)	86.16(4)	N(1)-C(1)-C(3)	107.41(24)
Cl(1′)-Mo-N(1)	80.22(7)	N(1)-C(1)-C(4)	107.26(24)
Cl(1′)-Mo-N(2)	93.15(9)	C(2)-C(1)-C(3)	110.1(3)
Cl(1′)-Mo-N(3)	159.73(9)	C(2)-C(1)-C(4)	112.7(3)
Cl(1)-Mo-Cl(2)	84.60(4)	C(3)-C(1)-C(4)	111.0(3)
Cl(1)-Mo-N(1)	73.56(6)	N(2)-C(5)-C(6)	105.4(3)
Cl(1)-Mo-N(2)	167.76(8)	N(2)-C(5)-C(7)	110.4(3)
Cl(1)-Mo-N(3)	85.15(9)	N(2)-C(5)-C(8)	109.8(3)
Cl(2)-Mo-N(1)	156.63(6)	C(6)-C(5)-C(7)	110.3(3)
Cl(2)-Mo-N(2)	96.06(8)	C(6)-C(5)-C(8)	110.6(3)
Cl(2)-Mo-N(3)	94.06(9)	C(7)-C(5)-C(8)	110.2(3)
N(1)-Mo-N(2)	103.53(10)	N(3)-C(9)-C(10)	106.9(3)
N(1)-Mo-N(3)	92.31(10)	N(3)-C(9)-C(11)	110.8(3)
N(2)-Mo-N(3)	106.96(12)	N(3)-C(9)-C(12)	107.2(3)
Mo-Cl(1)-Mo′	105.32(4)	C(10)-C(9)-C(11)	108.4(4)
Mo-N(1)-C(1)	127.12(17)	C(10)-C(9)-C(12)	112.0(5)
Mo-N(2)-C(5)	154.02(22)	C(11)-C(9)-C(12)	111.5(4)
Mo-N(3)-C(9)	172.42(23)		

two pyridines *trans* to the imido groups. The overall structure of **2** is closely related to that of $WCl_2(NPh)_2$(bipy) (bipy = α,α-bipyridine).[9] The geometry for the imido ligands of **2**, a short and linear imido bond (Mo-N(2) = 1.705(3) Å, Mo-N(2)-C(5) = 173.4(4)°), and a long and angular imido bond (Mo-N(1) = 1.736(4) Å, Mo-N(1)-C(1) = 163.8(4)°), is similar to that observed for **1**. The terminal Mo-Cl bond of **1**, 2.43 Å, and the average Mo-Cl bond of **2**, 2.42 Å, are significantly longer than that of $Mo(NAr')Cl_4$(thf) (Ar′ = p-tolyl, thf = tetrahydrofuran), 2.34 Å.[10] Hence the imido groups are bener π-donor ligands than the Cl ligands.

Deposition of Thin Films from 2

Although both **1** and **2** are volatile in vacuum, **2** has a greater vapor pressure and suffers less degradation than **1** when vaporized. Consequently, we chose **2** to investigate its potential as a single-source precursor to molybdenum nitride and molybdenum carbonitride thin films.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters of **2**

	x	y	z	Beq
Mo	0.88945(3)	0.90494(5)	0.50000	3.401(19)
C11	0.95181(10)	1.08167(19)	0.40028(11)	5.27(8)
C12	0.80453(10)	0.80081(18)	0.61333(11)	4.84(7)
N1	0.8645(3)	0.7740(5)	0.4198(3)	3.94(23)
N2	0.9769(3)	0.8504(5)	0.5467(3)	4.09(22)
N3	0.7718(3)	1.0466(5)	0.4595(3)	3.72(21)
N4	0.8898(3)	1.1206(5)	0.6003(3)	4.20(22)
C1	0.8622(4)	0.6422(6)	0.3637(4)	4.5(3)
C2	0.9333(5)	0.5445(8)	0.3814(5)	7.0(4)
C3	0.8635(5)	0.6972(10)	0.2687(5)	8.8(5)
C4	0.7871(5)	0.5577(9)	0.3856(7)	9.2(5)
C5	1.0552(4)	0.8031(7)	0.5763(4)	4.4(3)
C6	1.1033(4)	0.7548(11)	0.5000(8)	10.9(6)
C7	1.0473(5)	0.6807(11)	0.6422(7)	11.4(6)
C8	1.0968(5)	0.9325(10)	0.6202(9)	12.1(7)
C9	0.7170(3)	1.0945(7)	0.5173(5)	5.1(3)
C10	0.6517(4)	1.1752(7)	0.4933(7)	7.0(4)
C11	0.6408(4)	1.2110(8)	0.4066(6)	7.4(4)
C12	0.6954(4)	1.1635(7)	0.3469(5)	6.1(4)
C13	0.7593(4)	1.0804(7)	0.3755(4)	4.8(3)
C14	0.9050(4)	1.0951(8)	0.6855(4)	5.6(4)
C15	0.9086(5)	1.2031(9)	0.7482(4)	7.3(4)
C16	0.8927(5)	1.3480(9)	0.7225(5)	8.6(5)
C17	0.8770(4)	1.3776(7)	0.6362(6)	7.3(4)
C18	0.8772(4)	1.2613(7)	0.5767(4)	5.6(3)
H2A	0.934	0.514	0.441	7.9
H2B	0.981	0.599	0.369	7.9
H2C	0.932	0.457	0.344	7.9
H3A	0.908	0.752	0.257	9.5
H3B	0.816	0.755	0.259	9.5
H3C	0.861	0.611	0.230	9.5
H4A	0.743	0.624	0.371	10.5
H4B	0.786	0.533	0.445	10.5
H4C	0.783	0.472	0.349	10.5
H6A	1.109	0.837	0.459	11.9
H6B	1.078	0.674	0.470	11.9
H6C	1.154	0.725	0.519	11.9
H7A	1.021	0.600	0.614	12.7
H7B	1.018	0.718	0.689	12.7
H7C	1.099	0.653	0.659	12 7
H8A	1.069	0.964	0.668	12.9
H8B	1.104	1.010	0.578	12.9
H8C	1.149	0.897	0.637	12.9
H9	0.725	1.075	0.578	5.7
H10	0.613	1.206	0.536	7.8
H11	0.598	1.268	0.389	7.9
H12	0.687	1.185	0.285	6.6
H13	0.797	1.047	0.331	5.6
H14	0.914	0.997	0.704	6.2
H15	0.920	1.182	0.809	8.2
H16	0.895	1.426	0.763	8.8
H17	0.865	1.478	0.617	7.5
H18	0.870	1.282	0.514	6.5

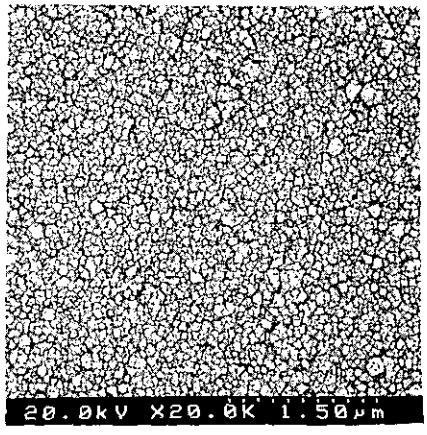
Table 4. Bond Distances and Bond Angles of 2

Bond Distance (Å)			
Mo-Cl(1)	2.4216(16)	C(1)-C(3)	1.518(10)
Mo-Cl(2)	2.4185(16)	C(1)-C(4)	1.510(10)
Mo-N(1)	1.736(4)	C(5)-C(6)	1.474(12)
Mo-N(2)	1.705(5)	C(5)-C(7)	1.484(10)
Mo-N(3)	2.430(5)	C(5)-C(8)	1.505(11)
Mo-N(4)	2.450(4)	C(9)-C(10)	1.364(9)
N(1)-C(1)	1.450(7)	C(10)-C(11)	1.361(14)
N(2)-C(5)	1.457(7)	C(11)-C(12)	1.357(11)
N(3)-C(9)	1.342(8)	C(12)-C(13)	1.377(9)
N(3)-C(13)	1.322(7)	C(14)-C(15)	1.353(9)
N(4)-C(14)	1.334(8)	C(15)-C(16)	1.377(12)
N(4)-C(18)	1.322(8)	C(16)-C(17)	1.357(12)
C(1)-C(2)	1.505(9)	C(17)-C(18)	1.373(9)
Bond Angle (°)			
Cl(1)-Mo-Cl(2)	161.48(6)	N(1)-C(1)-C(2)	110.2(5)
Cl(1)-Mo-N(1)	96.22(15)	N(1)-C(1)-C(3)	106.9(5)
Cl(1)-Mo-N(2)	93.91(16)	N(1)-C(1)-C(4)	107.4(5)
Cl(1)-Mo-N(3)	81.90(11)	C(2)-C(1)-C(3)	110.1(6)
Cl(1)-Mo-N(4)	82.72(12)	C(2)-C(1)-C(4)	109.9(6)
Cl(2)-Mo-N(1)	95.34(15)	C(3)-C(1)-C(4)	112.4(6)
Cl(2)-Mo-N(2)	96.24(16)	N(2)-C(5)-C(6)	110.0(5)
Cl(2)-Mo-N(3)	83.96(11)	N(2)-C(5)-C(7)	109.7(5)
Cl(2)-Mo-N(4)	82.20(12)	N(2)-C(5)-C(8)	109.6(5)
N(1)-Mo-N(2)	107.90(21)	C(6)-C(5)-C(7)	111.1(7)
N(1)-Mo-N(3)	88.60(18)	C(6)-C(5)-C(8)	108.3(7)
N(1)-Mo-N(4)	164.06(18)	C(7)-C(5)-C(8)	108.1(7)
N(2)-Mo-N(3)	163.36(18)	N(3)-C(9)-C(10)	123.4(7)
N(2)-Mo-N(4)	88.03(19)	C(9)-C(10)-C(11)	119.3(7)
N(3)-Mo-N(4)	75.49(14)	C(10)-C(11)-C(12)	118.4(6)
Mo-N(1)-C(1)	163.8(4)	C(11)-C(12)-C(13)	119.3(6)
Mo-N(2)-C(5)	173.4(4)	N(3)-C(13)-C(12)	123.4(6)
Mo-N(3)-C(9)	124.4(4)	N(4)-C(14)-C(15)	124.3(6)
Mo-N(3)-C(13)	119.4(4)	C(14)-C(15)-C(16)	117.5(7)
C(9)-N(3)-C(13)	116.2(5)	C(15)-C(16)-C(17)	119.5(6)
Mo-N(4)-C(14)	117.7(4)	C(16)-C(17)-C(18)	118.8(6)
Mo-N(4)-C(18)	125.3(4)	N(4)-C(18)-C(17)	122.8(6)
C(14)-N(4)-C(18)	117.0(5)		

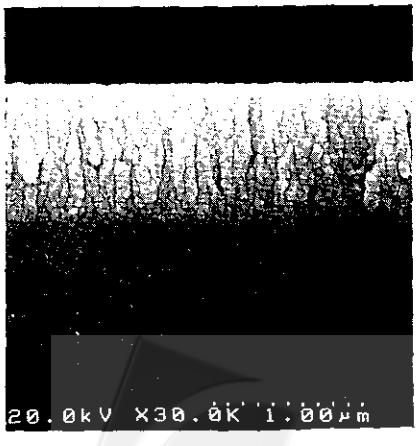
Deposition experiments at low pressure were conducted in a reactor constructed with a cold wall. Uniform gray and metallic lustrous thin films were grown on Si and glass substrates between 450 °C and 650 °C with hydrogen as carrier gas. Surface and cross-sectional scanning-electron micrographs of a typical thin film appear in Fig. 3. Growth rates, increased with increasing temperature of deposition, were 10 - 70 Å/min. The thin films were polycrystalline according to X-ray diffraction measurements. An exemplary diffraction pattern of a thin film deposited at 500 °C appears in Fig. 4. Major Cu K_α lines at angles 2θ equal to 37.21°, 43.25°, 62.69°, 75.09° and 79.20° are observed. These peaks are assigned respectively to (111), (200), (220), (311) and (222) reflections of a cubic structure with the lattice parameter, a, being 4.18 Å, near the lattice parameter of γ-Mo_2N, 4.16 Å, and also near that of Mo_2C, 4.14 Å. Our previous experience indicated that diffraction measurements alone cannot generally distinguish cubic phase metal nitride from cubic phase metal carbide or carbonitride.[3a-c]

The bulk elemental composition of the films was determined with wavelength-dispersive spectra (WDS). Molybdenum nitride thin films with small carbon concentrations were grown below 550 °C. For example, a film deposited at 500 °C had a composition $MoC_{0.06}N_{0.7}$. With increasing temperature of deposition, the N/Mo ratios decreased whereas the C/Mo ratios increased, yielding molybdenum carbonitride thin films. For example, a film grown at 650 °C had a composition $MoC_{0.5}N_{0.3}$. A similar behavior was observed in previous work of our group.[3c] The concentration of oxygen in the films was less than 5%, and that of chlorine was less than the detection limit of WDS.

Volatile products were identified to be H_2, CH_4,



(a)



(b)

Fig. 3. SEM photographs of a thin film deposited at 500 °C on Si; (a) surface and (b) cross-section.

CH_3CN, $Me_2C=CH_2$ and pyridine according to gas chromatography-mass spectrometry (GC-MS) and residual gas analysis (RGA). Pyridine likely dissociated from **2** at first because the py-Mo linkage, a dative bond, is expected to be the weakest bonding in **2**. Other volatile products are rationalized as decomposition products of $=NBu^t$ ligands. $Me_2C=CH_2$ appeared to be generated from γ-hydrogen activation of the $=NBu^t$ ligands, followed by dissociation of the C-N bond. The Mo-N link can be preserved in this process during growth of molybdenum nitride thin films. As indicated by formation of CH_4 and MeCN, another major decomposition pathway was β-methyl activation of $=NBu^t$ ligands. MeCN might form from removal of two methyl groups successively from the $=NBu^t$ ligand followed by breaking the Mo = N bond. The methyl fragments either underwent further C-H bond activation on the surface to generate carbon atoms and hydrogen atoms, or combined with surface hydrogen atoms to form CH_4. This process appears to account for incorporation of carbon atoms into the films. In the CVD process, there was no chlorine-containing product detected by GC-MS or RGA. As there was no chlorine atom detected in the films either, the fate of this element appeared to be mysterious. When the reactor was thoroughly inspected after each experiment, deposition of dark blue solid on the wall was observed. When an aqueous solution of the blue solid was reacted with a solution of silver nitrate, a white solid precipitated, indicating formation of AgCl. This preliminary result indicates that the dark blue solid was $MoCl_5$. Detailed examination is in progress.

EXPERIMENTAL SECTION

General Procedures for Preparations of 1 and 2

Chemicals and solvents were manipulated in a dry environment free of oxygen. $MoCl_2(NBu^t)_2(dme)$ (dme = dimethoxyethane) was synthesized according to a published route.[11]

^1H and ^{13}C NMR spectra were recorded using a Varian Unity-300 spectrometer. Mass spectra were measured on a spectrometer (Vacuum Generator Trio-3000) by the method of direct insertion. Elements were analyzed with a Heraeus CHN-O-Rapid Analyzer.

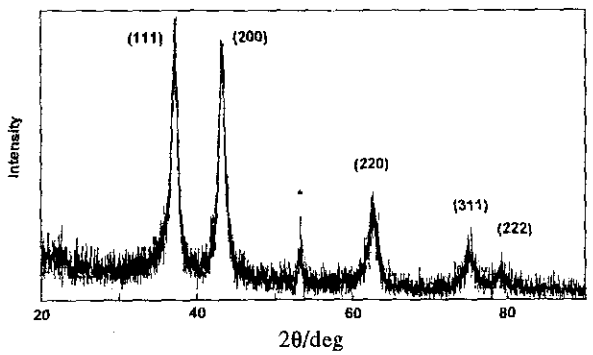


Fig. 4. X-ray diffraction pattern of a thin film deposited at 500 °C on Si; the signal marked by * is a reflection of the substrate.

Preparation of $[MoCl(\mu\text{-}Cl)(NBu^t)_2(NH_2Bu^t)]$, 1

To $MoCl_2(NBu^t)_2(dme)$ (1.05 g, 2.53 mmol) dissolved in hexane (80 mL), $^tBuNH_2$ (2 mL) was added slowly. An orange solid separated after the reaction mixture was stirred overnight (0.88 g, 93% based on Mo). Recrystallization from toluene at -15 °C gave large crystals suitable for X-ray structural analysis.

^1H NMR data recorded at 300 MHz in benzene-d_6 at +25 °C (all chemical shifts in ppm relative to Me_4Si) showed patterns assignable to two isomers, **a** and **b**: **a**, 1.13 (s, 9 H, Me_3CNH_2), 1.40 (s, 18 H, Me_3CN=), 2.69 (s br, 2 H, Me_3CNH_2). **b**, 1.04 (s, 9 H, Me_3CNH_2), 1.44 (s, 18 H, Me_3CN=), 4.81 (s br, 2 H, Me_3CNH_2). From integration ot the corresponding signals, the ratio of **a** to **b** was estimated to be 4:1.

^{13}C-{^1H} NMR data of a recorded at 75 MHz in benzene-d_6 at +25 °C (all chemical shifts in ppm relative to Me_4Si): 29.94 (Me_3CNH_2), 30.77 (Me_3CN=), 51.75 (Me_3CNH_2), 71.90 (Me_3CN=).

Mass spectrum (electron impact, ^{92}Mo): *m/z* 304 [M - $^tBuNH_2$]$^+$.

Anal. Calcd. (found) for $MoCl_2C_{12}H_{29}N_3$: C, 37.79 (37.46); H, 7.61 (7.72); N, 11.00 (10.72).

Preparation of $MoCl_2(NBu^t)_2(py)_2$, 2

To $MoCl_2(NBu^t)_2(dme)$ (1.01 g, 2.51 mmol) dissolved in hexane (50 mL), pyridine (4 mL) was added slowly. A pale orange solid precipitated immediately. After the reaction mixture was stirred overnight, the solid was collected (1.15 g, 98% based on Mo). Recrystallization from toluene at -15 °C gave large crystals suitable for X-ray structural analysis.

^1H NMR data recorded at 300 MHz in benzene-d_6 at +25 °C (all chemical shifts in ppm relative to Me_4Si): 1.50 (s, 18 H, Me_3CN=), 6.55 (m, 4 H, NCHC*H*), 6.84 (m, 2 H, NCHCHC*H*), 9.09 (d, 4 H, NC*H*).

^{13}C-{^1H} NMR data recorded at 75 MHz in benzene-d_6 at +25 °C (all chemical shifts in ppm relative to Me_4Si): 29.85 (Me_3CN=), 71.73 (Me_3CN=), 123.33 (NCHCH), 136.73 (NCHCHCH), 151.72 (NCH).

Table 5. Crystal Data Summary

	1	2
Formula,	$Mo_2Cl_4N_6C_{12}H_{58}$	$MoCl_2N_4C_{18}H_{28}$
F_w,	764.44	466.34
Space Group,	Triclinic P-1	Orthorhombic P $na2_1$
a(angstron),	8.897(4)	16.8604(24)
b(angstron),	10.518(3)	8.920(3)
c(angstron),	10.663(3)	15.120(3)
alpha(deg.),	107.684(23)	
β(deg.),	98.03(3)	
γ(deg.),	99.26(3)	
V(A**3),	919.3(5)	2274.1(9)
Z,	1	4
D_{calc}(g.cm^{-3}),	1.381	1.362
λ(Angstron),	0.7107	0.7107
F(000),	396.	960
Unit cell detn: #; (2θ range),	25; (20.74 - 31.26 deg.)	25; (16.84 - 29.24 deg.)
Scan type,	θ/2θ	θ/2θ
Scan width (deg),	2(0.70+0.35tan(θ))	2(0.70+0.35tan(θ))
Scan Speed (deg/min),	2.06-8.24	2.06-8.24
2θ(max),	50.0	50.0
h k l ranges,	(-9; 9)(0; 11)(-11; 11)	(0; 20)(0; 10)(0; 17)
μ(cm^{-1}),	9.811	8.082
Crystal size(mm),	0.25 × 0.50 × 0.50	0.20 × 0.40 × 0.50
Transmission,	0.878; 1.000	0.911; 1.000
Temperature,	298.00	298.00
# of meas. reflns,	3126	2075
# of obsed reflns (I > 2.0sig(I)),	2843	1575
# of unique reflns,	3115	2075
R_F; R_w,	0.023; 0.026	0.027; 0.025
GoF,	1.37	1.45
Refinement program,	NRCVAX	NRCVAX
# of atoms,	47	53
# of refined params,	164 (2843 out of 3115 reflns.)	226 (1575 out of 2075 reflns.)
Minimize function,	SUM(w|Fo-Fc|**2)	SUM(w|Fo-Fc|**2)
Weights scheme,		(1/σ(Fo))**2)
The weight modifier K in KFo**2 is,		0.000050
g (2nd. ext. coeff.) × 10**4,	0.534(16)	1.38(8)
(δ/σ)max,	0.0118	0.0329
(D-map)max,min e/A**3,	-0.260; 0.370	-0.220; 0.230

Mass spectrum (electron impact, ^{92}Mo): *m/z* 304 [M - 2 py]$^+$.

Anal. Calcd. (found) for $MoCl_2C_{18}H_{28}N_4$: C, 46.15 (46.32); H, 5.98 (5.63); N, 11.97 (11.72).

Structural Determinations

Data were collected and measured on a dilfractometer (Enraf Nonius CAD-4). Crystal data are summarized in Table 5.

1 Empirical formula: $C_{24}H_{58}N_6Cl_4Mo_2$, M = 764.44, triclinic, space group $P\bar{1}$, a = 8.897(4) Å, b = 10.518(3) Å, c = 10.663(3) Å, α = 107.68(2)°, β = 98.03(3)°, γ = 99.26(3)°, V = 919.3(5) Å^3, Z = 1, D_c = 1.381 g/mL, λ(Mo-K_α) = 0.7107 Å, F(000) = 396, μ = 9.81 cm^{-1}. Ψ scan absorption correction was made (T_{max} & T_{min}, 1.00 & 0.88 respectively). 3115 unique reflections were measured and 2843 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R = 0.023 and R_w = 0.026. Atomic parameters are presented in Table 1. Bond distances and bond angles are listed in Table 2.

2 Empirical formula: $C_{18}H_{28}N_4Cl_2Mo$, M = 466.34, orthorhombic, space group $Pna2_1$, a = 16.860(2) Å, b = 8.920(3) Å, c = 15.120(3) Å, V = 2274.1(9) Å^3, Z = 4, D_c = 1.362 g/mL, λ(Mo-K_α) = 0.7107 Å, F(000) = 960, μ = 8.08 cm^{-1}. Ψ scan absorption correction was made (T_{max} & T_{min},

1.00 & 0.91 respectively). 2075 unique reflections were measured and 1575 reflections with $I > 2\ \sigma(I)$ were used in the refinement. The refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R = 0.027$ and $R_w = 0.025$. Atomic parameters are presented in Table 3. Bond distances and bond angles are listed in Table 4.

CVD Experiments

Experiments on deposition of thin films were conducted in a home-made cold-wall reactor. The reactor was heated internally with a 650 W quartz-halogen lamp and evacuated with a diffusion pumping system. A U-trap installed between the reactor and the pumping system collected gaseous products at -196 °C. For each experiment, a base pressure 10^{-5} torr was obtained before the substrates were loaded under an Ar atmosphere. The reactor was evacuated again while it was heated to a temperature 50 °C above a desired temperature of deposition. After this procedure was completed, the reactor was allowed to cool to the desired temperature and **2** was vaporized into the reactor at 80 °C with hydrogen flowing at 10 sccm as the carrier gas. Deposition was performed at temperatures 450 - 650 °C for 3 h. After vaporization of **2** was terminated, the films were annealed for 30 min at the same temperature.

The morphology of the films was analyzed with a scanning-electron microscope (Hitachi S-4000). Bulk elemental composition of the films was investigated with wavelength dispersive spectra (JEOL JXA-733 spectrometer). Microstructure and crystallinity of the films were investigated with an X-ray diffractometer (MAC MXP-3) equipped with a thin-film attachment. Gaseous products collected in the experiments were analyzed by gas chromatography-mass spectrometry (Shimadzu GC-14A/QP 1000EX instrument). On-line analysis of the gas-phase products was performed using a residual gas analyzer (VG Quadruples Sensorlab 300D).

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Key Words

Molybdenum complex; Organoimido ligands; Chemical vapor deposition; Molybdenum nitride; Molybdenum carbonitride.

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