

Controlled Thermolysis of Nitrido- and Imidomolybdenum Complexes: A New Route to Phase-Pure Molybdenum Nitrides

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Received January 26, 1998. Revised Manuscript Received March 27, 1998

Nitridotris(neopentyl)molybdenum(VI) and its oxo-bridged bis(imido) derivative are suitable molecular precursor materials for bulk molybdenum nitrides. Temperature-programmed thermolysis in flowing ammonia yields bulk molybdenum nitrides in high purity. The presence of ammonia facilitates complete hydrocarbon elimination resulting in products with carbon contents below 0.1 wt %. A maximum heating rate of 0.5 °C/min between 100 and 200 °C is necessary to prevent an explosive decomposition of these complexes. The resultant product at 700 °C is phase-pure δ -MoN, as characterized by XRD and elemental analysis. γ -Mo₂N can be synthesized by simple variation of the thermolysis conditions: Annealing of the primary thermolysis product in inert gases (e.g., N₂, Ar) from 500 to 700 °C decreases the nitrogen content, with γ -Mo₂N resulting as the final phase. Oxygen contamination in the product, a major problem of common oxide-nitridation routes, is completely avoided by using this new synthetic approach.

Introduction

Transition metal nitrides have attracted scientific attention because of their often unusual electrical, magnetic, chemical, and mechanical properties. Especially molybdenum nitrides, as materials with significant catalytic properties, have gained growing interest in the last 10 years. There has been an increasing number of reports on molybdenum nitrides as heterogeneous catalysts for several hydrotreating reactions in petrochemical processes,¹ NH₃ synthesis,² ethane hydrogenolysis,³ CO hydrogenation,⁴ and even catalytic decomposition of hydrazine in satellite microthrusters.⁵ In many of these cases, molybdenum nitrides can be used as alternatives to rare, expensive noble metal catalysts. Unfortunately, the synthesis of molybdenum nitrides (γ -Mo₂N as well as δ -MoN) usually requires high temperatures (700–1000 °C) and/or high-pressure reactions between molybdenum powder or molybdenum oxides and nitrogen, N₂/H₂ mixtures, or ammonia.^{6,7} These methods often lead to materials with impurities

of mainly oxygen or the parent metal, which can entail detrimental effects on the catalytic properties.

It was our intention to design alternative synthetic routes to bulk molybdenum nitrides from *molecular* organometallic precursor compounds. However, very little is known about the decomposition pathways of organometallic complexes. While there are some examples for the ammonolysis of transition metal dialkylamides giving nitrides as powders or thin films,⁸ the use of organometallic nitrides as precursors, a class of compounds which already contains the correct ratio of atoms needed in the transition metal nitride, is hardly known so far.

The first example for this concept was the conversion of [(*t*-BuCH₂)₂TaN]₅ to cubic TaN by Wolczanski et al.,⁹ which demonstrates the potential of organometallic nitrides as single-source precursors for transition metal nitrides.

We have investigated the thermolysis of nitridotris(neopentyl)molybdenum(VI), **1**, and its oxo-bridged bis(imido) derivative **2** in flowing ammonia and nitrogen to produce molybdenum nitrides.

Air and moisture-stable **1** is easily accessible from N≡Mo(O-*t*-Bu)₃.¹⁰ In the solid state it is kinetically stabilized against nucleophilic attack by the linear

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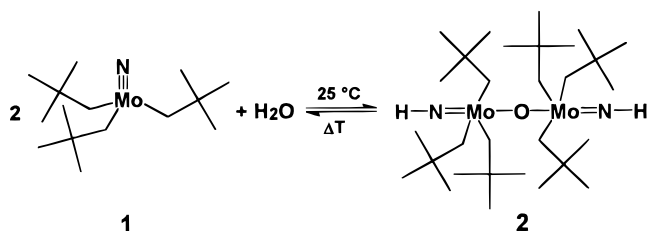


Figure 1. Reaction of $\text{Np}_3\text{Mo}\equiv\text{N}$ with water; Np = neopentyl.

$\text{Mo}\equiv\text{N}\rightarrow\text{Mo}$ coordination and steric shielding by the relatively bulky neopentyl ligands. **1** reacts with water to give the oxo-bridged bis(imido) complex **2** by virtue of a quantitative cross-addition (Figure 1).

Experimental Section

Organometallic complexes were synthesized according to published procedures.¹⁰ High-temperature reactions were performed in a quartz tube furnace, type ROK/A 4/60, with a thermocontrol unit, type RE 1.1 (Heraeus Instruments). Organometallic compounds (200–300 mg) were placed in a porcelain boat in the middle of a quartz tube, which was twice evacuated before heating to prevent oxygen contamination. Ammonia (99.998%, Messer) was dried over MgClO_4 and injected into the quartz tube at ca. 100 sccm via a gas-flow controller unit (Fischer & Porter). Temperature programs for thermolysis consisted of two major heating rates: 0.25–4 °C/min in the range from 100 to 200 °C, and 3 °C/min from 200 to 700 °C, followed by an isothermal treatment at 700 °C for 1 h. The resulting nitride powders were evacuated for half an hour at 500 °C for removal of adsorbed ammonia and stored under a N_2 atmosphere. Thermogravimetric analysis was obtained by use of a Mettler Toledo Star System thermobalance under a dinitrogen flow of 25 sccm and a heating rate of 10 °C/min. A computer-controlled Huber Diffraktionstechnik X-ray powder diffractometer, type G 642, with a copper source and a monochromator system was used for characterization of the nitrides. Samples were mounted on backless aluminum sample holders using an amorphous polypropylene foil and silicon grease. Data were compared to JCPDS catalog values for identification.¹¹ X-ray diffraction peak widths of the most intense peak in the diffraction pattern were taken to approximately determine crystallite sizes in the solid products. Therefore, the Debye–Scherrer equation,¹²

$$d_{hkl} = K\lambda/b \cos \theta$$

was used, where K is taken as unity, b is the corrected peak width at half-maximum in terms of goniometer angle 2θ , λ is the incident radiation wavelength (1.5402 Å), θ is the angle of diffraction, and d_{hkl} is the dimension of coherently reflecting domains in the $\langle hkl \rangle$ direction.

Elemental analyses of the reactants and products were performed by the Microanalytical Laboratory at the Anorganisch-chemisches Institut der Technischen Universität München. Nitrogen, hydrogen, and carbon contents were determined by combustion methods; molybdenum was determined photometrically as $\text{Mo}(\text{SCN})_5$ complex.

Results and Discussion

Nitridotris(neopentyl)molybdenum(VI) **1** shows unique thermal properties. TG analysis indicates that it decom-

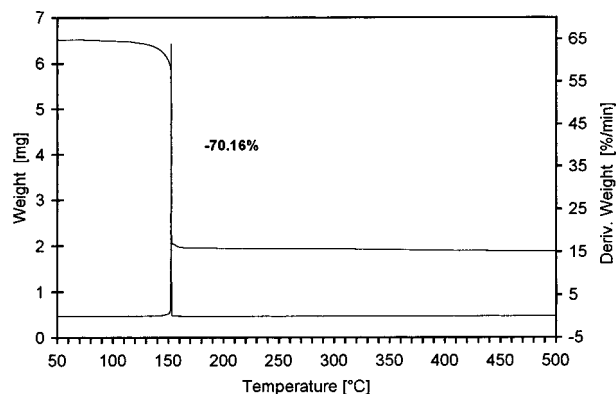


Figure 2. Thermogram of $\text{Np}_3\text{Mo}\equiv\text{N}$ showing weight loss (left) and derivative weight loss (right).

poses explosively upon heating at about 150 °C in only one single step (see thermogram in Figure 2), losing predominantly neopentane. The resulting black powders show very low contents of C and H, corresponding to a loss of hydrocarbon fragments of more than 90 wt %.

The dimeric complex **2** shows identical thermal behavior, because it splits off water at temperatures below 100 °C.¹³ This is remarkable, because it indicates that the molybdenum–oxygen bond in the bis(imido) complex is rather weak, leading to a complete thermal reversibility of the water addition reaction (Figure 1).

Their unique decomposition profiles make nitridotris(neopentyl)molybdenum(V) and its dimeric imido derivative good potential precursors for molybdenum nitride.

Ammonia is known to facilitate the elimination of hydrocarbons from organometallic compounds and to suppress the incorporation of carbon into transition metal nitrides.¹⁴ In fact, thermolysis of bulk **1** in flowing ammonia at temperatures from 100 to 700 °C leads to δ -MoN powders of high purity, as proved by XRD and elemental analysis.¹⁵ The carbon content in the thermolysis products (see Table 1) is strongly dependent on the heating rate in the temperature range 100–200 °C. Only heating rates below 0.5 °C/min gave carbon-free, highly pure δ -MoN in a continuous, non-explosive decomposition reaction. Higher heating rates lead to incomplete hydrocarbon elimination with carbon contaminations up to 2 mass % C in the final product. Figure 3 shows the X-ray diffraction pattern of the thermolysis product of complex **1** with a heating rate of 0.25 °C/min.

Low heating rates in the range 100–200 °C are also required for nonexplosive decomposition of the complexes, indicating that ammonia facilitates hydrocarbon elimination by opening a new pathway for the reaction. Isolation of the evolved reaction gases in a dry ice/methanol trap and characterization by gas chromatography/mass spectrometry yielded neopentane and pivalonitrile as the main gaseous products.

According to this, we postulate that ammonia as a strong Lewis base breaks up the linear $\text{Mo}\equiv\text{N}\rightarrow\text{Mo}$

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Table 1. Synthesis of Molybdenum Nitrides from Molecular Precursors: Temperature Conditions and Analytical Data

precursor ^a	product ^b	heating rate ^c (°C/min)	elemental analysis (wt %)				d_{hkl} ^d (nm)
			Mo	N	C	H	
Np ₃ Mo≡N	δ-MoN	4	87.3	11.5	1.9	0.2	24.6
Np ₃ Mo≡N	δ-MoN	3	n.d. ^e	13.5	0.55	0	41.2
Np ₃ Mo≡N	δ-MoN	0.5	86.8	13.0	<0.1	0	21.8
Np ₃ Mo≡N	δ-MoN	0.25	87.1	13.2	<0.1	0	24.4
(Np ₃ MoNH) ₂ O	δ-MoN	0.5	87.3	12.4	<0.1	0	20.1
(Np ₃ MoNH) ₂ O	δ-MoN	0.25	n.d.	13.4	<0.1	0	31.7
(Np ₃ MoNH) ₂ O	γ-Mo ₂ N	0.5	91.8	6.9	1.0	0.7	11.3
Np ₃ Mo≡N	γ-Mo ₂ N	0.25	91.2	7.1	0.3	0.8	9.3

^a Np = neopentyl. ^b According to XRD. ^c At 100–200 °C. ^d $d_{(200)}$ for δ-MoN, $d_{(111)}$ for γ-Mo₂N. ^e n.d. = not determined.

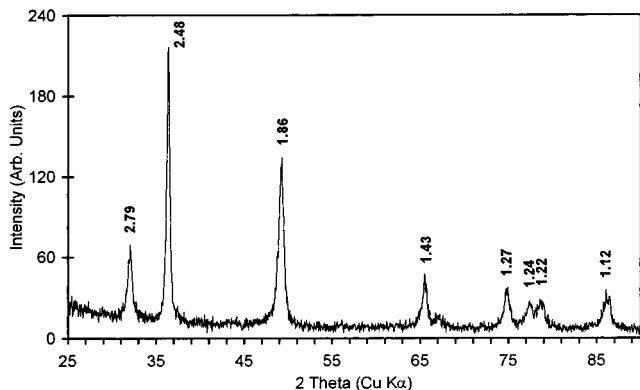


Figure 3. Powder X-ray diffraction of δ-MoN formed by thermolysis of Np₃Mo≡N in ammonia with a heating rate of 0.25 °C/min. Labels give the measured d spacings in angstroms (Å).

chain, coordinates at the Mo center, and induces a sequence of neopentane eliminations via β-hydrogen abstraction. Finally, pivalonitrile is liberated and “MoN” is left in the residue. (Because of the extreme dilution of the reaction gases in ammonia, the neopentane/pivalonitrile ratio could not be quantified.)

While there is a strong influence of the heating rate on the carbon content, we have found that the crystallite sizes are nearly independent from the thermolysis heating rates. In almost all cases the $d_{(200)}$ values of the nitrides lie in the range of 20–25 nm (see Table 1).

To complete our study of the synthesis of molybdenum nitrides from molecular organometallic molybdenum compounds, we also tried to approach γ-Mo₂N via thermolysis of the complexes **1** and **2**. Nitrides with lower N contents are usually accessible by annealing amorphous nitrides with higher N contents at elevated temperatures. To produce γ-Mo₂N, the fcc phase of molybdenum nitride, we stopped the thermolysis experiments in flowing ammonia at 500 °C, a temperature at which the products were not yet crystalline according to XRD, and continued the temperature-programmed thermolysis in the presence of nitrogen or argon gas. This resulted in a decrease of the N content of the primary thermolysis products and formation of the cubic γ-Mo₂N lattice (see Figure 4).

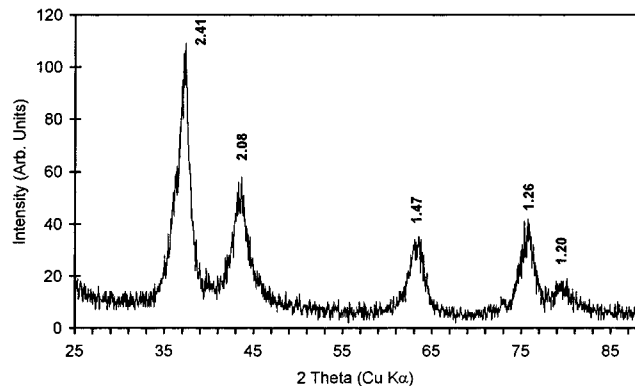


Figure 4. Powder X-ray diffraction of γ-Mo₂N formed by thermolysis of Np₃Mo≡N in ammonia up to 500 °C and nitrogen from 500 to 700 °C. Labels give the measured d spacings in angstroms (Å).

The C contents of the products again depend on the heating rate in the range 100–200 °C, but they are slightly higher (see Table 1). This effect indicates that hydrocarbon elimination in ammonia was not complete at 500 °C. Crystallite sizes are smaller than in the δ-MoN products with $d_{(111)}$ values at about 10 nm.

Concluding Remarks

Temperature-programmed thermolysis of peralkylated nitrido- and imidomolybdenum complexes in flowing ammonia contributes a new, efficient route to phase-pure molybdenum nitrides. The composition and phase of the nitride can be controlled by variation of external synthesis parameters such as heating rates and reaction gases. A major advantage of this precursor route is products without oxygen, chlorine, or sulfur contaminations, which would otherwise seriously hamper the catalytic performance of these materials.

Acknowledgment. We thank the Bayerische Forschungsverbund Katalyse (FORKAT) for financial support of this work. The authors are also grateful to Dr. K. Wernthaler and Dr. J. Graefe from SKW Trostberg AG for helpful discussions.

CM9800433