Synthesis of Transition-Metal Nitrides from Nanoscale Metal Particles Prepared by Homogeneous Reduction of Metal Halides with an Alkalide

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Received November 1, 1996. Revised Manuscript Received March 18, 1997[⊗]

Transition-metal nitrides have been synthesized by heating nanoscale metal particles under flowing N_2(g) or NH_3(g). In some cases reaction temperatures are significantly lower than those required by conventional heating procedures. Nanoscale metal particles of Mo, Nb, Ta, Fe−Mo, Fe−Nb, and Cu−Nb were prepared by reduction of the respective metal chloride or mixture of chlorides with the sodide, $[K^+(15\text{-crown-}5)_2]Na^-$, in dimethyl ether solution. The previously characterized nitrides that were prepared (with synthesis conditions indicated) include γ-Mo_2N (800 °C, N_2) and Mo_2N (720 °C, N_2), Ta_3N_5 (650 °C, NH_3), Fe_3Mo_3N (>650 °C, N_2), and a mixture of niobium nitride phases (800 °C, N_2). A previously unreported phase has been found in the Ba−Nb−N system.

Introduction

Nanometer-size metal particles are scientifically and technologically important, in part because their high surface area leads to high reactivity. Numerous methods for the preparation of (1−20 nm diameter) nanoscale metal particles[1] have been reported, including (1) chemical reductions with borohydrides,[2] alkali metal or aromatic radical anions,[3] hydrogen,[4] and various mild reductants;[5] (2) matrix isolation (solvated metal atom dispersion); (3) evaporation of metals;[6] (4) chemical vapor deposition;[7] (5) thermal decomposition of a precursor;[8] and (6) sol−gel processes.[9] Some uses of these reactive metal particles include organometallic synthesis,[3] degrading chlorocarbons in contaminated water supplies,[10] and catalysis.[11]

The rapid homogeneous reduction of transition-metal salts dissolved in dimethyl ether (Me_2O(l)) or tetrahydrofuran (THF) by dissolved alkalide[12] or electride[13] was recently shown to produce metal particles with diameters from <3 to 15 nm. A major advantage of using an alkalide or electride is that their strong reducing power (∼−3 V) allows rapid reduction of soluble metal salts to the metallic state and intermetallic compounds or alloys[14] can be produced from homogeneous solutions. While numerous transition-metal and main-group metal particles and alloys have been synthesized by this new method, it is still a challenge to synthesize particles of extremely oxophilic metals such as Nb, Mo, or Ta devoid of surface oxidation. However, particles of less oxophilic metals (e.g., Au, Cu, Te, and Pt) have been synthesized with little or no surface oxidation.[12]

We wondered if the small size and high reactivity of nanometer-size metal particles of Nb, Mo, and Ta might enable them to react at low temperature with N_2(g) or NH_3(g) to form nitrides. Although some transition-metal nitrides can be prepared at relatively low temperature by reacting a chloride[15] or oxide[16] with ammonia gas, preparations directly from the metal usually require high temperatures[17] (e.g., $T \geq 1200$ °C for NbN and TaN) and produce specimens with very low surface areas, a detriment for their potential use either for catalysis or as solid-state synthesis precursors. We report here the synthesis of some transition-metal nitrides from nanoscale metal particles.

Experimental Section

1. Chemicals. 15-Crown-5 (Aldrich, 98%), potassium metal (M.S.A. Research Corp.), sodium metal, dimethyl ether,

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

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S0897-4756(96)00565-0 CCC: $14.00

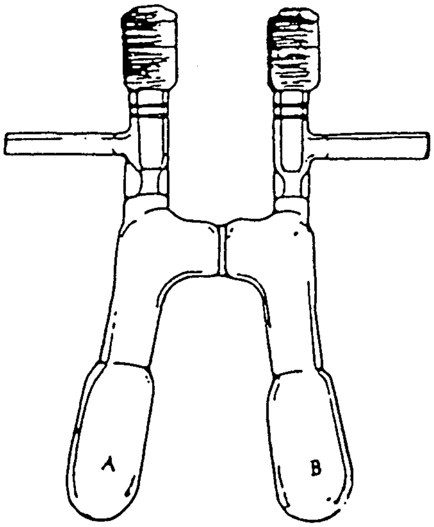

Figure 1. An H-cell.

ammonia (Matheson), $NbCl_5$ (Johnson Matthey, grade 1), $MoCl_5$ (Aldrich, 99.99%), $TaCl_5$, $FeCl_3$ (Fisher, purified), $CuCl_2$ (Aldrich, 99.99%).

2. Reagent Purification. *15-Crown-5* was distilled.

Dimethyl ether was distilled from solutions that contained excess Na−K and benzophenone and was stored in a stainless steel vessel.

$NH_3(g)$ was condensed over sodium metal and stored in a stainless steel vessel.

$TaCl_5$ dissolved in dimethyl ether in an H-cell (Figure 1) fitted with a medium frit[18] gave a cloudy solution that became clear after filtration. The chloride was regenerated by evaporating the ether.

$FeCl_3$ was sublimed.

$N_2(g)$ was purified by molecular sieves (Aldrich) to remove moisture and by De-Ox catalyst (Johnson-Matthey) to remove O_2.

$NH_3(g)$ was obtained by vaporizing $NH_3(l)$.

3. Preparation of Nanoscale Metal Particles. Nanoscale metal particles were prepared by a modification of the procedure of Dye and Tsai.[12] The sodide, $[K^+(15\text{-crown-}5)_2]\text{-}Na^-$, replaced the potasside, $[K^+(15\text{-crown-}5)_2]K^-$, as the reducing reagent. The basic reactions are

$$\text{Na−K} + 2\,(15\text{-crown-}5) \xrightarrow{\text{Me}_2\text{O(l)}} [\text{K}^+(15\text{-crown-}5)_2]\text{Na}^- \quad (1)$$

$$2\text{MCl}_x + x[\text{K}^+(15\text{-crown-}5)_2]\text{Na}^- \xrightarrow{\text{Me}_2\text{O(l)}} 2\text{M} + x[\text{K}^+(15\text{-crown-}5)_2]\text{Cl}^- + x\text{NaCl} \quad (2)$$

In an Ar-filled glovebox the appropriate amount of metal chloride or a mixture of two metal chlorides and a small stirring bar were added into one side of a previously evacuated H-cell fitted with a medium frit[18] (Figure 1). Into the other side of the H-cell the appropriate amount of Na−K(l) (molar ratio of Na:K = 1:1) and 15-crown-5 were added together with a small stirring bar. *This sample loading procedure must be completed as quickly as possible because some of the Na−K and 15-crown-5 react immediately upon contact and the formed sodide decomposes equally rapidly at room temperature.* To minimize alkalide decomposition, the H-cell was quickly removed from the glovebox, chilled to −60 °C with an isopropyl alcohol−dry ice bath, and maintained at that temperature. The cell was evacuated to 10^{-5} Torr and purified $Me_2O(l)$ was distilled into both sides of the cell as quickly as possible. Na−K alloy reacts immediately with 15-crown-5 in $(CH_3)_2O(l)$ to form a brownish-blue solution of the soluble alkalide, $[K^+(15\text{-crown-}5)_2]Na^-$. The H-cell was normally maintained in the dry ice bath overnight to enable the Na−K alloy and 15-crown-5 to react completely. The next day, while keeping the H-cell cold, the alkalide solution was poured, in several steps, through the frit into the metal salt solution. A homogeneous reduction reaction occurs immediately to form the black powder product.

The byproducts, $[K^+(15\text{-crown-}5)_2]Cl^-$ and NaCl, were removed by washing the product first with $Me_2O(l)$ and then with $NH_3(l)$. Intermediate grinding of the powder product during washing is necessary to break up cluster aggregates. Since some reduction of the organic complexant and/or solvent occurs, traces of ammonia-insoluble organic compounds remain in the product.[12,14] These impurities could usually be removed by heating the products to 500 °C under high vacuum for about 3 h.

Mo Metal Particles. Typically 0.717 g of Na−K alloy (11.5 mmol of Na, 11.5 mmol of K), 5.308 g of 15-crown-5 (24.1 mmol), and 0.633 g of $MoCl_5$ (2.32 mmol) were used for the reduction reaction.

Nb Metal Particles. Typically 0.588 g of Na−K alloy (9.47 mmol of Na, 9.47 mmol of K), 4.250 g of 15-crown-5 (19.3 mmol), and 0.831 g of $NbCl_5$ (3.08 mmol) were used for the reaction.

Ta Metal Particles. Na−K alloy (0.344 g, 5.54 mmol of Na, 5.54 mmol of K), 2.493 g of 15-crown-5 (11.1 mmol), and 0.693 g of $TaCl_5$ (1.93 mmol) were used for the reduction.

Fe−Mo Metal Particles. Na−K alloy (0.581 g, 9.36 mmol of Na, 9.36 mmol of K), 4.259 g of 15-crown-5 (19.3 mmol), 0.249 g of $FeCl_3$ (1.54 mmol), and 0.419 g of $MoCl_5$ (1.53 mmol) were used.

Fe−Nb Metal Particles. Na−K alloy (0.596 g, 9.60 mmol of Na, 9.60 mmol of K), 4.357 g of 15-crown-5 (19.8 mmol), 0.258 g of $FeCl_3$ (1.59 mmol), and 0.435 g of $NbCl_5$ (1.61 mmol) were used.

Cu−Nb Metal Particles. Na−K alloy (0.623 g, 10.0 mmol of Na, 10.0 mmol of K), 4.461 g of 15-crown-5 (20.3 mmol), 0.258 g of $CuCl_2$ (1.92 mmol), and 0.516 g of $NbCl_5$ (1.91 mmol) were used.

4. Nitride Synthesis. Alundum (Al_2O_3) containers were heated at 900 °C under vacuum for several hours to remove H_2O and other volatile contaminants. All preparatory manipulations were performed in an Ar-filled glovebox whose typical moisture and oxygen contents were <0.5 and <1 ppm, respectively.

(1) Mo_2N. Mo particles confined in the alundum boat were heated in flowing $N_2(g)$. Different samples were heated at 800 °C for 5 h and at 720 °C for 20 h, respectively.

(2) NbN_x (x = 0.95, 0.98, 1) Nb particles were heated in flowing $NH_3(g)$ first at 700 °C for 4 h and then at 860 °C for 8 h.

(3) Ta_3N_5. Ta particles were heated in flowing $NH_3(g)$ at 650 °C for 8 h.

(4) Fe_3Mo_3N. Fe−Mo particles were heated either in flowing $N_2(g)$ or $NH_3(g)$ at various temperatures between 400 and 980 °C.

(5) Ba−Nb−N System. The Nb particles, mixed with Ba_3N_2 in the approximate Ba:Nb = 2:1 molar ratio, were heated in flowing $N_2(g)$ at 720 °C for 20 h.

(6) Fe−Nb System. Various samples of the Fe−Nb metal particles were heated at 500 and 800 °C in $NH_3(g)$, 600 and 800 °C in $N_2(g)$.

(7) Cu−Nb System. Different samples of the Cu−Nb metal particles were heated under flowing $N_2(g)$ or $NH_3(g)$ at various temperatures: 355, 420, 600, and 700 °C.

5. Analysis. The presence of metal elements with zero oxidation state and elemental Cl, Na, and K were detected with a Perkin-Elmer PHI 5400 ESCA/XPS spectrometer. Specimens were examined with a Nicolet 740 FT-IR spectrometer to check for the presence of organic impurities. Specimen crystallinity was detected by X-ray powder diffraction. All prepared metal particles were examined by Guinier X-ray powder diffraction with monochromatic Cu Kα_1 radiation in a 114.6 mm Guinier camera. NBS certified Si (a = 5.43082(3) Å) served as internal standard. Intensity data were collected with a Philips APD diffractometer system with Cu Kα radia-

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[18] "Double Tube" from Kontes, Vineland, NJ 08360.

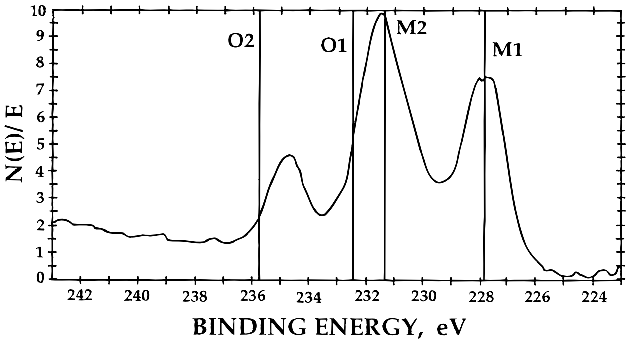

Figure 2. XPS spectrum of Mo metal particles. Peak are assigned as M1 → metallic Mo $3d_{5/2}$, M2 → metallic Mo $3d_{3/2}$, O1 → MoO_3 $3d_{5/2}$, O2 → MoO_3 $3d_{3/2}$.

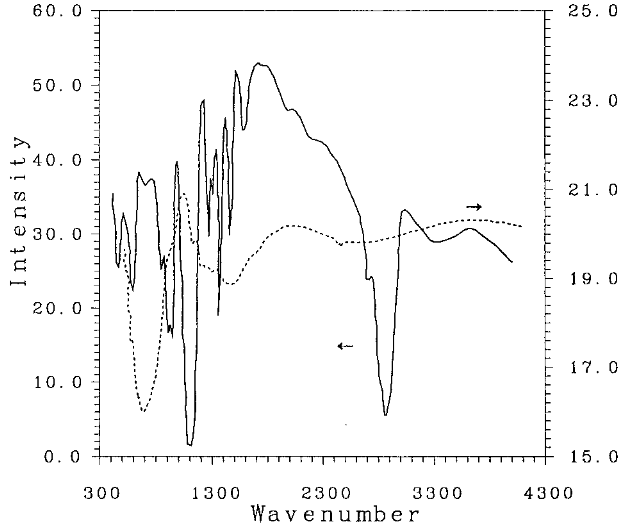

Figure 3. Solid line (left ordinate): IR spectrum of Mo particles prior to the heat treatment. Dashed line (right ordinate): IR spectrum of Mo particles after the heat treatment.

tion. The programs VISSER,[19] TREOR5,[20] and DICVOL92[21] were used to index powder patterns of some of the products. The program LAZY PULVERIX[22] was used for intensity calculations.

Results and Discussion

1. Metal Particles. All of the metal particles prepared as described above are black powders that catch fire upon exposure to air. The XPS spectrum of Mo particles shown in Figure 2 indicates the presence of Mo^0; it also shows that surface oxidation has occurred. The spectrum does not show any peaks assignable to Cl^-, K^+, or Na^+, suggestive that these elements were removed from the product by the washing procedure.

Guinier X-ray powder patterns did not show any reflections for metal products before or after the heat treatment, suggestive both that metal particles are very small and that byproducts such as crystalline NaCl were removed, consistent with the XPS data.

The FTIR spectrum (Figure 3, solid line) for Mo metal particles shows that some organic impurities cannot be removed by washing with $Me_2O(l)$ and $NH_3(l)$. Most of the IR peaks, however, disappeared after the sample was subject to heat treatment at 500 °C (Figure 3, dashed line). The fact that metal particles can still catch fire upon exposure to air after this heat treatment indicates their high level of reactivity. Heat treatment up to 500 °C is essential to remove most of the volatile impurities. Even after this heat treatment, additional volatile impurities may still be released when the particles are heated between 700 and 800 °C under flowing $N_2(g)$. To minimize the loss of reactivity that might occur upon heating in vacuum, pretreatment temperatures were limited to <510 °C.

Table 1. Solubilities of Some Alkali-Metal Halides in $NH_3(l)$ at 0 °C (g/100 g of Solution)[37]

cation	Cl^-	Br^-	I^-
Li^+	1.43		
Na^+	11.37	29.00	56.88
K^+	0.132	21.18	64.81
Rb^+	0.289	18.23	68.15
Cs^+	0.381	4.38	60.28

Use of the sodide $K^+(15\text{-crown-}5)_2]Na^-$, instead of potasside, $K^+(15\text{-crown-}5)_2]K^-$, as a reducing agent forms NaCl instead of KCl as byproduct when a transition-metal chloride is a reactant. NaCl is much more soluble than KCl in $NH_3(l)$ as shown by the data in Table 1. This greater solubility significantly reduces the time spent on product washing.

As is shown in Table 1, the solubilities of many alkali-metal iodides and bromides in liquid ammonia are much greater than that of NaCl. So from the product point of view, use of a transition-metal iodide or bromide should facilitate product purification. On the other hand, a homogeneous reduction reaction requires a high or moderately high solubility of the transition-metal salt in the $Me_2O(l)$ solution. Dye and Tsai[23] reported minimal solubility of MoI_2 in $Me_2O(l)$ (<0.005 mol dm^{-3}). We tried to prepare Mo particles from $MoBr_3$, but it did not dissolve in either $Me_2O(l)$ or THF even after purification by sublimation.

An additional advantage of using the sodide $K^+(15\text{-crown-}5)_2]Na^-$ as a reductant is that the Na−K alloy is a liquid and $NH_3(l)$ pretreatment[12] is not necessary, thereby shortening the preparative time and reducing the potential for oxidation of the alkali metal. The Na−K liquid alloy is also easier to manipulate than the sticky potassium metal.

2. Nitrides. *(1) Mo_2N.* The X-ray powder diffraction reflections are assignable to two single-phase modifications of molybdenum nitride, γ-Mo_2N and Mo_2N.[24] The reflections of both nitride forms are rather broad, indicative of small particle sizes. MoN was not observed under the reaction conditions employed, consistent with some previous reports. Lyutaya[25] reported that nitriding activated Mo metal with NH_3 at 450 °C yielded MoN, while nitriding at 700 °C produced Mo_2N. Jaggers and co-workers[26] also reported Mo_2N to be the favored modification at higher temperatures.

(2) NbN_x. After the Nb particles were heated in flowing NH_3 at 700 °C for 4 h, the X-ray powder pattern

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showed several very broad reflections which could be assigned to an oxide nitride phase with the formula $NbN_{0.6}O_{0.3}$.[27] The oxygen may result from surface oxidation of the extremely oxophilic metal particles. To get a better crystallized product, the obtained oxide nitride was reheated in flowing NH_3 at 860 °C for 8 h. The Guinier X-ray pattern shows that the oxide nitride was converted into mixed Nb nitride phases.[24] With the exception of one very weak reflection, all diffraction lines can be assigned[24] to three nitride phases, $NbN_{0.95}$,[28] $NbN_{0.98}$,[29] and NbN.[30] Variability of stoichiometry is common for many transition-metal binary nitrides[17] in which metal atoms form a closest packed structure and nitrogen atoms fill interstitial positions.

Conversion of oxide nitrides to nitrides has also been observed by Lyutaya[25] and Stacy et al.[26] They observed an oxide nitride intermediate MoO_xN_{1-x} during the reaction of MoO_3 with NH_3. According to the studies of DiSalvo and co-workers,[16] the free energy for converting niobium oxide to the nitride in NH_3(g) at 1000 K is −80.8 kJ/mol, indicative that niobium nitride should be preparable by reacting an oxide precursor with ammonia gas.

(3) Ta_3N_5. The *d* spacings obtained by the Guinier technique for Ta_3N_5[24] match well those calculated by using reported atomic positions of Ta_3N_5.[31]

(4) Fe_3Mo_3N. This air stable compound was initially reported by zur Loye and co-workers.[32] Our X-ray powder pattern of Fe_3Mo_3N[24] is almost identical with that reported. The cubic lattice parameter (a = 11.0848(5) Å) agrees with the reported value.[32]

The reaction between Fe−Mo particles and gaseous N_2 or NH_3 was studied at various temperatures. On the basis of the highly reactive nature of the metal particles, the nitride Fe_3Mo_3N was probably synthesized at a significantly lower temperature (<500 °C) than those employed in this work, but Guinier X-ray powder diffraction shows no crystallinity for specimens formed below 600 °C under either flowing NH_3 or N_2. The X-ray powder diffraction data suggest that annealing at 650 °C under an NH_3 atmosphere is necessary to form crystalline Fe_3Mo_3N detectable by X-ray diffraction, while a temperature higher than 700 °C is necessary to get the well-crystallized nitride by the nanoscale metal particle procedure.

(5) Fe−Nb System. This system showed the most complexity. When the metal particles were heated at 600 °C under flowing N_2, the Guinier powder X-ray pattern only showed several unidentifiable reflections.[24] Literature data for all reported iron and niobium nitrides and oxides, iron−niobium carbides and oxides, and iron−niobium alloys were checked in an effort to identify the powder pattern. But none of these data matches the reflections listed. We do not know if a new nitride phase or a mixture of new phases is produced. When the metal particles were heated at 800 °C under nitrogen, a different powder pattern was observed.[24] In this case, $NbN_{0.95}$[28] and α-Fe[33] metal were identified. There is a third as yet unidentified phase in the product to which the program TREOR5[20] assigned an orthorhombic cell with a = 12.7638 Å, b = 6.2248 Å, c = 5.0112 Å, and FM = 17;[34] one of the 13 observed reflections remains unindexed. The coexistence of Fe metal and $NbN_{0.95}$ would seem to preclude the third phase being an iron niobium ternary nitride; it might be a new niobium nitride modification.

Table 2. Interplanar *d* Values, Miller Indices, and Observed Intensities for the New Phase Found in Ba−Nb−N System

no.	d_0	d_c	h	k	l	I_0
1	8.1432	8.1306	1	0	0	44
2	5.6585	5.6577	0	0	1	24
3	4.0666	4.0653	2	0	0	26
4	3.9438	3.9401	0	2	0	21
5	3.6119	3.6129	2	1	0	44
6	3.5473	3.5457	1	2	0	79
7	3.3756	3.3740	−2	0	1	21
8	3.2332	3.2333	0	2	1	100
9	3.1021	3.1016	−2	1	1	48
10	3.0306	3.0313	−1	2	1	57
11	2.9922	2.9913	2	1	1	50
12	2.9796	2.9783	1	2	1	95
13	2.8295	2.8288	0	0	2	44
14	2.7104	2.7098	−1	0	2	27
15	2.5634	2.5628	−2	2	1	27
16	2.2071	2.2063	2	3	0	18
17	1.9688	1.9682	4	1	0	20
18	1.9146	1.9145	3	0	2	52
19	1.8862	1.8859	0	0	3	22
20	1.8347	1.8344	4	1	1	2

(6) Cu−Nb System. Jacobs and Zachwieja prepared $CuTaN_2$ by heating pressed pellets of CuI + $NaTaN_2$ under flowing N_2 at 400 °C.[35] Cu_3N was reported to decompose to Cu and N_2 at 470 °C with an enthalpy of −83.7 kJ mol^{-1}.[36] We thought the ternary copper niobium nitride analogue might be preparable at a relatively low temperature from Cu−Nb nanoscale metal particles. Two different samples of Cu−Nb metal particles were heated under flowing NH_3 at 355 °C for 24 h and 600 °C for 43 h, respectively. In both cases the reaction yielded Cu metal and an unidentified phase. Since copper is easily reduced by H_2, two different samples were heated under flowing N_2 at 420 °C for 3 days and 700 °C for 15 h, respectively. At 420 °C only single-phase Cu was observed on the Guinier X-ray powder pattern, indicative that the Cu nanoscale particles had sintered to form particles whose size was large enough for detection by powder X-ray diffraction. However, the Nb metal or the Nb-containing product still had a very small particle size. After treatment at 700 °C, another as yet unidentified phase in addition to the Cu phase was observed. These reactions suggest that if a Cu−Nb nitride phase does form, it cannot be detected by X-ray powder diffraction.

(7) Ba−Nb−N. A green compound with trace unknown impurities was obtained by heating a mixture

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[27] Powder diffraction file card 13-467. JCPDS: International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

[28] Powder diffraction file card 25-1361. JCPDS: International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

[29] Powder diffraction file card 34-337. JCPDS: International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

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of Ba_3N_2 and Nb (nanoscale particles) under flowing N_2 at 720 °C. The compound releases NH_3 upon contact with air. It does not dissolve in $(CH_3)_2O(l)$, THF, CH_3NH_2, CH_3CN, CH_3OH, and $NH_3(l)$, but most of the trace impurities can be removed by washing it with CH_3OH. The Guinier X-ray powder pattern was indexed by the programs TREOR5,[20] VISSER,[19] and DICVOL92[21] based on a monoclinic cell with lattice parameters $a = 8.137(2)$ Å, $b = 7.883(1)$ Å, $c = 5.672(2)$ Å, $\beta = 92.54(2)°$, M(20) = 44, F(20) = 70. The indexed results are compiled in Table 2; the structure remains under investigation.

Conclusion

Homogeneous reduction of metal chlorides by an alkalide in dimethyl ether solution produces highly reactive nanoscale metal particles. These particles can be used as precursors for the synthesis of transition-metal nitrides. Several previously known transition-metal nitrides, γ-Mo_2N (800 °C, N_2) and Mo_2N (720 °C, N_2), Ta_3N_5 (650 °C, NH_3), Fe_3Mo_3N (>650 °C, N_2), and $NbN_{0.95}$ (800 °C, N_2), as well as new but uncharacterized phases in the Ba−Nb−N, Fe−Nb−N, and Cu−Nb−N systems have been prepared. This work shows that these nanoscale metal particles are suitable precursors for the synthesis of microscale quantities of binary or ternary metal nitrides where both metals are transition elements. This synthesis method may prove useful for the preparation of new transition-metal-containing nitride phases, that when characterized may be preparable by other procedures or when specimens with very large surface areas are desired.

The procedure used to purify the nanoscale particles needs to be further improved. The organic impurities present in the particles interfere with the synthesis reaction when the very electropositive metals such as the alkali or alkaline earths are used as reactants because these metals are more sensitive to the organic impurities than are the transition metals. A method more sensitive than X-ray powder diffraction is also needed to examine the reaction products. The need to heat specimens at temperatures >500 °C to obtain detectable crystallinity precluded examining them for reaction at lower temperatures. We believe that nitride formation occurred in most specimens at temperatures far below those reported herein. Nevertheless, this work does demonstrate that nanoscale metal particles show promise as reactants for synthesis efforts when reactive metal precursors are needed.

Acknowledgment. J.L.D. and S.H.E. acknowledge numerous helpful discussions with Professor F. J. DiSalvo.

Supporting Information Available: Tables with observed interplanar *d* spacings and assigned literature values and one figure—the powder pattern of Fe_3Mo_3N (7 pages). Ordering information is given on any current masthead page.

CM960565N