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Magnesium and Calcium Nitrides as Nitrogen Sources in Metathetical Reactions To Produce Metal Nitrides

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Reaction of Ca_3N_2 or Mg_3N_2 with anhydrous metal chlorides ($MnCl_2$; MCl_3, M = Ti, V, Mo, Nd, Sm, Gd, Tb, Er; MCl_4, M = Hf, W; MCl_5, M = Nb, Ta) in evacuated sealed Pyrex or quartz ampules at 500−900 °C or by filament initiation under nitrogen or argon was used to produce metal nitrides and calcium or magnesium chloride. The nitrides were purified by washing with methanol and isolated in ca. 70−90% yield. Variation in reaction conditions allowed the isolation of intermediate phazes of Ln_2Cl_3N (Ln = Sm, Gd, Tb, Er) and Ca_2NCl, giving evidence that at least some of the reactions proceed via ionic metathesis pathways. Phase-pure VN and V_2N were produced, both of which have previously been inaccessible in solid-state reactions using metathetical methods.

Introduction

Most metals form nitrides. Transition metal nitrides have often been referred to as interstitial compounds as they share many properties with the metals (electrical conductivity, Hall coefficient, magnetic susceptibility, and heat capacity) and the nitrogen atoms occupy octahedral holes in a close-packed or related lattice.[1,2] They have found utility for their various properties of hardness, wear resistance, refractory nature, chemical inertness, low-temperature superconductivity, and catalytic activity.[1,3] Lanthanide nitrides form with the NaCl (*Fm*3*m*) structure and are often nonstoichiometric in nitrogen or occluded metal with the physical properties determined by the degree of nitrogen vacancy.[4]

Metal nitrides are conventionally made by the high-temperature combination of nitrogen, ammonia, or hydrogen/nitrogen mixture with the metal or its oxide or chloride, typically at temperatures of around 1000 °C over long time periods.[5] Problems with these preparations include the huge energy costs, incorporation of unreacted metal in the product and lack of control over crystallinity and particle sizes. These difficulties have inspired a great deal of work on alternative synthetic routes.

Bulk synthesis of nitrides include precursor decomposition and various self- propagating reactions. Precursor decomposition has tended to employ amides, either in unimolecular reactions or with ammonia as a coreactant. The use of ammonia is aimed at reducing intramolecular rearrangements with concomitant metal−carbon bond formation which are considered responsible for carbon incorporation.[6] Carbon-free precursors have been developed which lead, on thermolysis to a metal nitride.[7] Self-propagating high-temperature synthesis (SHS)[8] involves the initiation of an elemental combination reaction in an intimate mixture of elements, the reaction being sufficiently exothermic to become self-sustaining. In nitride synthesis, nitrogen is introduced either at elevated pressure in gaseous or liquid form or as sodium azide, where the sodium is vaporized during reaction. Complete conversion to metal nitride requires a significant fraction of nitride added to the reagent mixture and a high nitrogen pressure (10 MPa).[9]

Solid-state metathesis (SSM) reactions, whereby a metal halide is combined with, for example, an alkali-metal chalcogenide, can lead to the rapid formation of a wide variety of materials. These have included chalcogenides,[10,11] oxides,[12] pnictides,[13,14] silicides,[15] and nitrides.[16−19] A related technique has recently been

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employed for the synthesis of nanoparticulate materials from solution phase metathesis reactions.[20] Solid-state metathesis reactions can be initiated by a hot electric filament or heating in a sealed ampule and have a number of features in common including rapidity, exothermicity, controlled crystallinity in the products (by adding a diluent), and extreme exothermicity with temperatures often in excess of 1000 °C. The driving force is the coproduction of alkali-metal halide with its large lattice energy. SSM reactions can also be used to synthesize mixed-metal pnictides and metal mixed pnictides.[13] In nitride formation Li_3N,[16,17] NaN_3,[17,18] and lithium and sodium amides[19] have been used as nitrogen sources. The use of lithium and sodium amides, with the milder conditions they allow, has made possible the synthesis of more thermally sensitive phases such as Ta_3N_5 and Zn_3N_2.[19] The use of Ca_3N_2 in the preparation of ternary calcium metal nitrides has been reported by DiSalvo and co-workers.[21]

The mechanism operating in SSM reactions has been proposed as operating from one of two extremes,[13,14,16] reductive recombination (eq 1) or direct ionic metathesis (eq 2). Reductive recombination proceeds via reduction

$$MCl_n + Li_nE \rightarrow M + E + nLiCl \rightarrow ME + nLiCl \quad (1)$$

$$\begin{gathered} MCl_n + Li_nE \rightarrow M^{n+} + E^{n-} + nLiCl \rightarrow ME + nLiCl \\ M = \text{transition metal or lanthanide;} \\ E = N, P, As, S, Se, Te \end{gathered} \quad (2)$$

to the elements followed by a recombination promoted by the high temperature of the reaction. In ionic metathesis no reduction to the elements would occur and the reaction would proceed by the exchange of ions, possibly promoted by a melt of LiCl.

Recent reports[15] have given evidence that some metathetical reactions may proceed at least in part by reductive recombination. Thermolysis of rare-earth-metal chlorides with magnesium silicide produced rare-earth silicides, but a reduction in thermolysis time yielded mixtures with significant quantities of silicon. These data suggest a reductive recombination type mechanism. In the filament initiated reaction of $TiCl_3$ with Li_3N, titanium metal is detected as a minor phase along with TiN.[17] By altering the reaction ratios to include a mixture of NaN_3 and Li_3N, the degree of nitridation has been improved and only TiN is produced, suggesting a reductive recombination type mechanism, more nitrogen being produced by NaN_3. It is unlikely that traces of Ti can be accounted for by thermal decomposition of TiN as it has a decomposition temperature of 2950 °C and the maximum theoretical temperature (T_{ad}) or observed temperatures in these reactions is 1408 °C.[17] In thermally initiated reactions in sealed glass ampules, no elemental titanium was observed in the nitride, which showed good metal-to-nitrogen stoichiometry.[16]

Table 1. XRD Data for Lanthanide Nitrides Formed in Thermally Initiated Reactions

reagents	reaction conditions	product	lattice parameter **a**/Å (ref 23 **a** parameter)
$NdCl_3/Ca_3N_2$	500 °C/15 h	NdN	5.14 (5.14)
$SmCl_3/Mg_3N_2$	900 °C/cool	SmN	5.04 (5.04)
$SmCl_3/Ca_3N_2$	900 °C/cool	SmN	5.04 (5.04)
$GdCl_3/Mg_3N_2$	900 °C/cool	GdN	4.99 (4.99)
$GdCl_3/Ca_3N_2$	500 °C/15 h	GdN	5.00 (4.99)
$TbCl_3/Mg_3N_2$	900 °C/cool	TbN	4.92 (4.93)
$TbCl_3/Ca_3N_2$	500 °C/15 h	TbN	4.93 (4.93)
$ErCl_3/Mg_3N_2$	900 °C/cool	ErN	4.84 (4.84)
$ErCl_3/Ca_3N_2$	500 °C/15 h	ErN	4.83 (4.84)

In this paper the reactions of magnesium and calcium nitride with lanthanide and transition-metal chlorides are presented. These offer a facile route to metal nitrides, give some insight as to the reaction pathways that may be adopted in self-propagating reactions and enable a number of nitride phases that have been inaccessible from Li_3N or NaN_3 reactions to be isolated.

Experimental Section

All reagents were handled under either a nitrogen or argon atmosphere using either a Saffron Scientific glovebox or Schlenk line techniques. Anhydrous lanthanide and transition-metal chlorides and magnesium and calcium nitrides were obtained from Strem Chemicals or Aldrich Chemical Co. and used as supplied. All reagents were checked for phase and elemental purity by X-ray powder diffraction (XRD) and energy-dispersive X-ray analysis (EDXA) prior to use. Methanol was distilled over magnesium and iodine and degassed with nitrogen prior to use. A programmable tube furnace or a resistive electric filament was used to initiate the reactions. Quartz or Pyrex ampules (typically made with 2 mm thick walls and an internal volume of 15 cm^3) were annealed prior to use and thoroughly dried by flame under vacuum. The filament reactions were initiated by a resistive nicrome wire filament at ca. 800–900 °C. Photographs of the filament initiated reaction were recorded at 0.7 s intervals using Ilford XP2 film. XRD measurements were performed on a Siemens D5000 diffractometer in transmission mode using germanium monochromated Cu Kα_1 (λ = 1.5406 Å) radiation. Scanning electron microscopy (SEM) was carried out with a JEOL JSM820 instrument; EDXA was performed with a Kevex Quantum Detector Delta 4 with Quantex 6.2 software; this setup enables semiquantitative analysis for oxygen and allows analysis for elements with atomic numbers greater than 5.[22] Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 205 instrument using pressed KBr disks. Microanalysis was performed by the departmental service by combustion with tin powder.

Reactions by Thermal Initiation. Magnesium or calcium nitride (1–2 mmol) and anhydrous metal chloride (1:2 ratio of alkaline earth to chloride) were ground together in an agate pestle and mortar in a nitrogen-filled glovebox and placed in a quartz or Pyrex ampule which was sealed under vacuum. The ampule was placed in a furnace at room temperature and then rapidly brought (5–10 min) to either 500 or 900 °C, kept at the required temperature as detailed in Tables 1 and 2, and then allowed to cool (ca. 10 °C/min) to room temperature. The ampule contained a fused black solid which was opened in air, and the contents were washed with methanol (2 × 30 mL) and dried in vacuo. The products were identified by XRD (Tables 1 and 2), SEM/EDXA, FT-IR, and microanalysis. Microanalysis (from Ca_3N_2 at 900 °C); SmN, N 7.6%, (8.5%); HfN, N 6.6% (7.3%); Mn_4N, N 5.8% (6.0%); C and H levels were below 0.2% in all samples.

Filament Initiation. Reagents were ground together with an agate pestle and mortar, as above. Initiation was carried out with an electrically heated nicrome wire filament (800–

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Table 2. Products of Thermally Initiated Reactions of Transition Metal Chlorides with Magnesium and Calcium Nitride[a]

reagents		conditions	products
$TiCl_3$	Mg_3N_2	500 °C/15 h	TiN, Mg_3N_2, $TiCl_3$
		900 °C/cool	TiN
	Ca_3N_2	500 °C/15 h	TiN
		900 °C/cool	TiN
$HfCl_4$	Mg_3N_2	900 °C/cool	HfN
	Ca_3N_2	900 °C/cool	HfN
VCl_3	Mg_3N_2	500 °C/15 h	VN (poorly crystalline)
		900 °C/cool	VN
	Ca_3N_2	900 °C/cool	VN, V_2N
$TaCl_5$	Mg_3N_2	500 °C/15 h	Ta_2N, TaN (poorly crystalline)
	Ca_3N_2	500 °C/15 h	Ta_2N, TaN
$MoCl_3$	Mg_3N_2	500 °C/15 h	Mo
	Ca_3N_2	500 °C/15 h	Mo
WCl_4	Mg_3N_2	500 °C/15 h	W
	Ca_3N_2	500 °C/15 h	W
$MnCl_2$	Ca_3N_2	500 °C/15 h	Mn_4N (poorly crystalline)

[a] $MgCl_2$ and $CaCl_2$ omitted. Lattice parameters within 0.01 Å of lit.[23] values.

Table 3. Products of Filament-Initiated Reactions[a]

reagents		propagation	products
$TiCl_3$	Mg_3N_2	none	
	Ca_3N_2	fast	TiN, Ca_2NCl_3, Ca_3N_2
	$1Ca_3N_2$:$2Mg_3N_2$	none	
VCl_3	Mg_3N_2	none	
	Ca_3N_2	fast	V_2N, VN
	$1Ca_3N_2$:$2Mg_3N_2$	slow	V_2N
$NbCl_5$	Mg_3N_2	none	
	$1Ca_3N_2$:$2Mg_3N_2$	slow	Nb_2N, NbN
$TaCl_5$	Mg_3N_2	none	
	$1Ca_3N_2$:$2Mg_3N_2$	slow	Ta_2N (TaN)
$MoCl_5$	Mg_3N_2	slow	Mo
WCl_4	Mg_3N_2	slow	W

[a] $MgCl_2$ and $CaCl_2$ omitted. Lattice parameters within 0.01Å of lit.[23] values.

900 °C) in the agate mortar under either a dry nitrogen or argon atmosphere within a glovebox. The products were then washed, dried and characterized (Table 3) as for the thermally initiated products.

Caution. Self-propagating reactions are by nature very exothermic and on occasion produce large amounts of dinitrogen gas. If the reactions are contained within a small ampule, an explosion can occur. It is recommended that all reactions be carried out behind a blast-proof safety screen and the maximum pressure be calculated before performing sealed ampule reactions.

Results and Discussion

The reactions of magnesium and calcium nitrides with lanthanide and transition-metal chlorides were investigated. The reactions were thermally initiated in sealed evacuated glass ampules or initiated with an electrically heated filament. Products were generally obtained as loosely fused masses and some sublimation of salt such as $MgCl_2$ or $CaCl_2$ was observed coated onto the reaction vessel walls. Washing with methanol removed the coproduced $MgCl_2$, $CaCl_2$, Ca_2NCl, and any remaining reagents.

Characterization primarily involved X-ray powder diffraction and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDXA). The phases observed by XRD are discussed later in this section. SEM micrographs of purified products generally revealed aggregates on the micron scale of sharp featured particles (Figure 1). The crystallite sizes as determined by the Scherrer equation[24] based on the XRD line widths were of the order of 500 Å. EDXA was performed over several points on different grains to ensure consistency and, where Tables 1–3 indicate nitride phases only, metal and nitrogen were the sole elements detected. Magnesium or calcium and chlorine must, therefore, have been present at below the detection threshold of the method (approximately 0.5% for these elements). Nitrogen was only observed for first row transition elements (Figure 2), presumably because the "soft" X-rays it produces are absorbed too strongly in the case of the heavier elements. The instrument used is capable of resolving oxygen and nitrogen (with detection threshold around 1%), although oxygen was not observed by EDXA in the products. In other metathetical preparations of metal nitrides the incorporation of oxygen has proved problematic[10] and has been directly related to the oxygen contamination in the starting materials. FT-IR spectroscopy of the metal nitrides showed only a low intensity broad band centered around 450 cm^{-1} assignable to M–N vibrations. Microanalysis showed slightly nitrogen-deficient materials; the lower values could be due to some contamination with oxygen or the formation

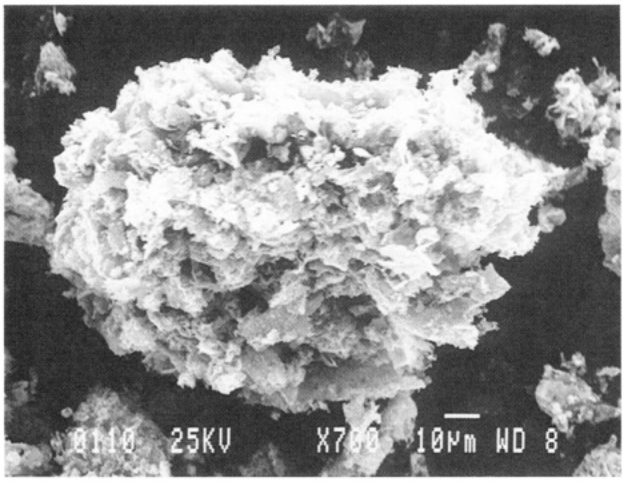

Figure 1. SEM micrograph of purified TiN produced from the reaction of $TiCl_3$ with Ca_3N_2.

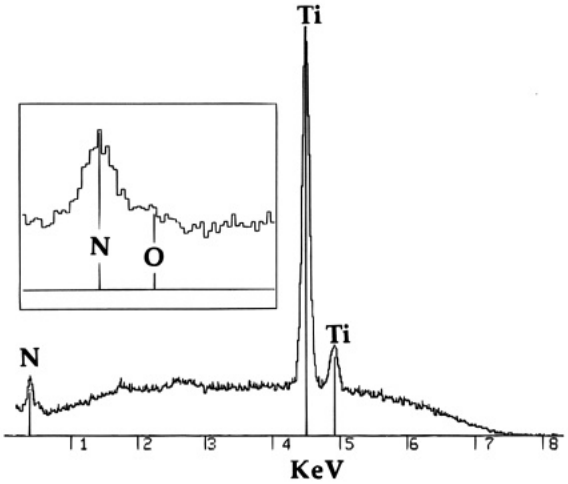

Figure 2. EDXA spectrum of purified TiN produced from the reaction of $TiCl_3$ with Ca_3N_2.

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(23) PDF-2 database, International Centre for Diffraction Data, Swarthmore, PA 19081, 1993.

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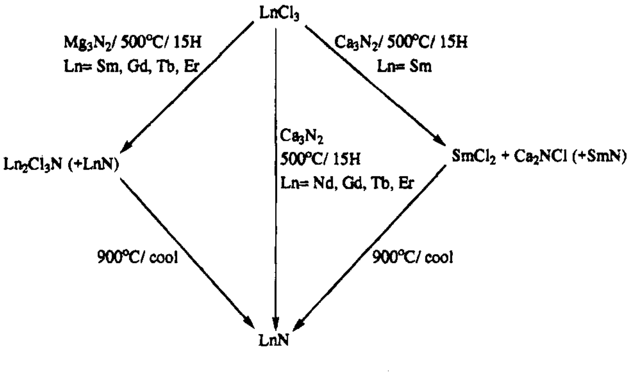
Scheme 1. Products of Reactions of Lanthanide Chlorides with Magnesium and Calcium Nitride



of a nonstoichiometric phase inconsistent with the XRD measurements. However, complete combustion is difficult to achieve in such refractory materials as metal nitrides[13,17] (mp > 2500 °C[5]), and the slightly low nitrogen levels are likely due to analytical difficulties.

Reactions with Lanthanide Chlorides. The powder XRD patterns of the products of reactions of magnesium and calcium nitride with lanthanide chlorides are represented in Table 1. A general trend is observed (Scheme 1) of reactions of calcium nitride occurring more readily than those of magnesium nitride. The main barrier to reaction can be expected to be solid-state diffusion. Calcium nitride decomposes at 900 °C, whereas magnesium nitride melts at 1500 °C, which would mean that propagation occurs more readily, once initiated, in the calcium case. Another explanation comes from examination of the reaction energetics (eqs 3 and 4).[25] The reactions of lanthanide chlorides with magnesium nitride are actually slightly endothermic (although entropy favored[26]).

$$\mathrm{GdCl_3} + {}^1/_2\mathrm{Mg_3N_2} \rightarrow \mathrm{GdN} + {}^3/_2\mathrm{MgCl_2} \qquad \Delta H_\mathrm{r}^\circ = +41\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

$$\mathrm{GdCl_3} + {}^1/_2\mathrm{Ca_3N_2} \rightarrow \mathrm{GdN} + {}^3/_2\mathrm{CaCl_2} \qquad \Delta H_\mathrm{r}^\circ = -202\ \mathrm{kJ\ mol^{-1}} \quad (4)$$

In both reactions (eqs 3 and 4) the rates are not typical of solid state metathesis reactions which are often complete in 1−2 s.[10,12] Heating of a mixture of lanthanide chloride and either magnesium or calcium nitride to 900 °C for 1 h formed only lanthanide nitride and magnesium or calcium chloride. Reducing the reaction time to ca. 10 min at 900 °C enables a trace of Ln_2Cl_3N to be observed in most reactions while reaction of Ca_3N_2 and $LnCl_3$ for 2 h at 500 °C produces LnN, Ca_2NCl, and Ln_2Cl_3N. Reaction of magnesium nitride under the same conditions predominantly yielded Ln_2Cl_3N and some $MgCl_2$ and a small amount of an unidentified phase (Figure 3a). The implications of these results will be discussed below.

Reactions with Transition Metal Chlorides. Products of the thermally initiated reactions of magnesium and calcium nitride with transition metal chlorides are summarized in Table 2. The greater ease of reaction of calcium over magnesium nitride is demonstrated by examination of the products with $TiCl_3$ at 500 °C. The calcium nitride reaction goes to completion within 15 h, whereas some reagents are observed in the products of the magnesium nitride reaction performed with the same conditions. No intermediates were observed in any of these reactions. This does not necessarily imply a process different from that occurring with the lanthanides, where Ca_2NCl and Ln_2Cl_3N were observed, it could be due to a faster reaction after initiation. The transition-metal chlorides generally have lower melting/decomposition temperatures than the lanthanide chlorides, and thus the solid-state diffusion barrier to activation will be reduced. The reactions are also more exothermic (eqs 3−6),[24] which would make propagation of the transition-metal reactions more favorable than those of the lanthanides after initiation.

$$\mathrm{TiCl_3} + {}^1/_2\mathrm{Mg_3N_2} \rightarrow \mathrm{TiN} + {}^3/_2\mathrm{MgCl_2} \qquad \Delta H_\mathrm{r}^\circ = -345\ \mathrm{kJ\ mol^{-1}} \quad (5)$$

$$\mathrm{TiCl_3} + {}^1/_2\mathrm{Ca_3N_2} \rightarrow \mathrm{TiN} + {}^3/_2\mathrm{CaCl_2} \qquad \Delta H_\mathrm{r}^\circ = -588\ \mathrm{kJ\ mol^{-1}} \quad (6)$$

The reaction of VCl_3 with Mg_3N_2, at 500 or 900 °C, produces phase-pure VN. VN produced from VCl_3 with Li_3N, NaN_3, or Ca_3N_2 is always contaminated with V_2N.[16,18] Only by using VCl_4 (a poisonous and corrosive liquid) has phase-pure VN been isolated from a metathesis reaction. This is a useful development as the VCl_3 provides a simple one-stage preparation (without having to handle VCl_4) of this potentially important heterogeneous catalyst.[1] The reactions of $MoCl_3$ and WCl_4 with calcium and magnesium nitride yielded Mo and W metals. Molybdenum and tungsten nitrides decompose below 790 °C (Mo_2N[5]), less than the temperatures expected during the reactions.

Filament Initiation. Some of the reactions studied could also be initiated by touching the reaction mixture with an electrically heated metal filament. No initiation or propagation was found to be possible with the lanthanide chlorides. The reaction products and the ease of propagation are summarized in Table 3. No changes in reactivity or composition of products was observed using an argon atmosphere instead of nitrogen. Under air, reactions were more vigorous and products were found to contain substantial amounts of oxide (of the order of 30%) in addition to the same nitride phase.

Filament-initiated reactions of Ca_3N_2 and Mg_3N_2 with transition metal chlorides showed different rates of propagation. Reactions of magnesium nitride with niobium or tantalum chloride could be initiated at the tip of the filament, but the reaction failed to propagate through the solid. Similar reactions with calcium nitride were easily initiated and spread through the whole reaction mixture very quickly. Reaction times were less than a second and accompanied by a bright thermal flash indicating a temperature of the order of 1000 °C. The reactions cool rapidly and approach ambient temperature in about 30 s. Using mixtures of Mg_3N_2 and Ca_3N_2, it was possible to modulate the reactions such that only a slow propagation occurred. This is demonstrated in Figure 4, which contains photographs of a slow propagation wave with a velocity of ca. 1 cm s^{-1} generated by a reaction of VCl_3 with a 1:2 mixture of Ca_3N_2 and Mg_3N_2. It is to be expected

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(25) Calculated from Hess' law using data from *Materials Thermochemistry*, 6th ed., Kubaschewski, O., Alcock, C. B., Spencer, P. J.; Pergamon: Oxford, 1993.

(26) The entropy for the reaction taking values for $LaCl_3$ and LaN at room temperature and without taking into account any phase changes gives $\Delta S_\mathrm{r} = 11$ J $\mathrm{deg^{-1}\ mol^{-1}}$.

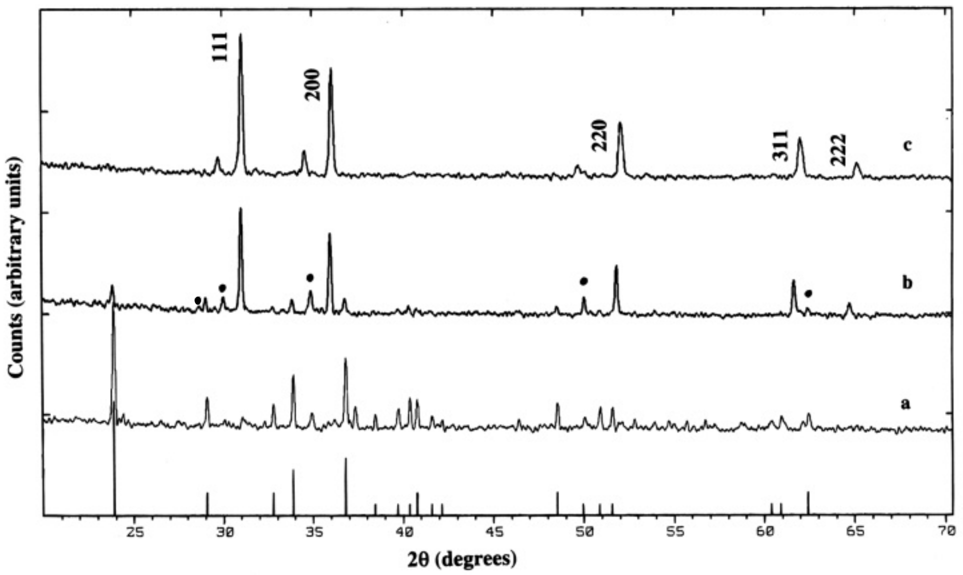

Figure 3. XRD patterns of the crude products of reactions of (a) $GdCl_3$ with Mg_3N_2 heated for 2 h at 500 °C, (b) $GdCl_3$ with Mg_3N_2 heated at 900 °C, and (c) $TbCl_3$ with Mg_3N_2 heated at 900 °C. Stick pattern represents Gd_2Cl_3N,[23] bold circles represent $MgCl_2$, indexed lines for LnN.

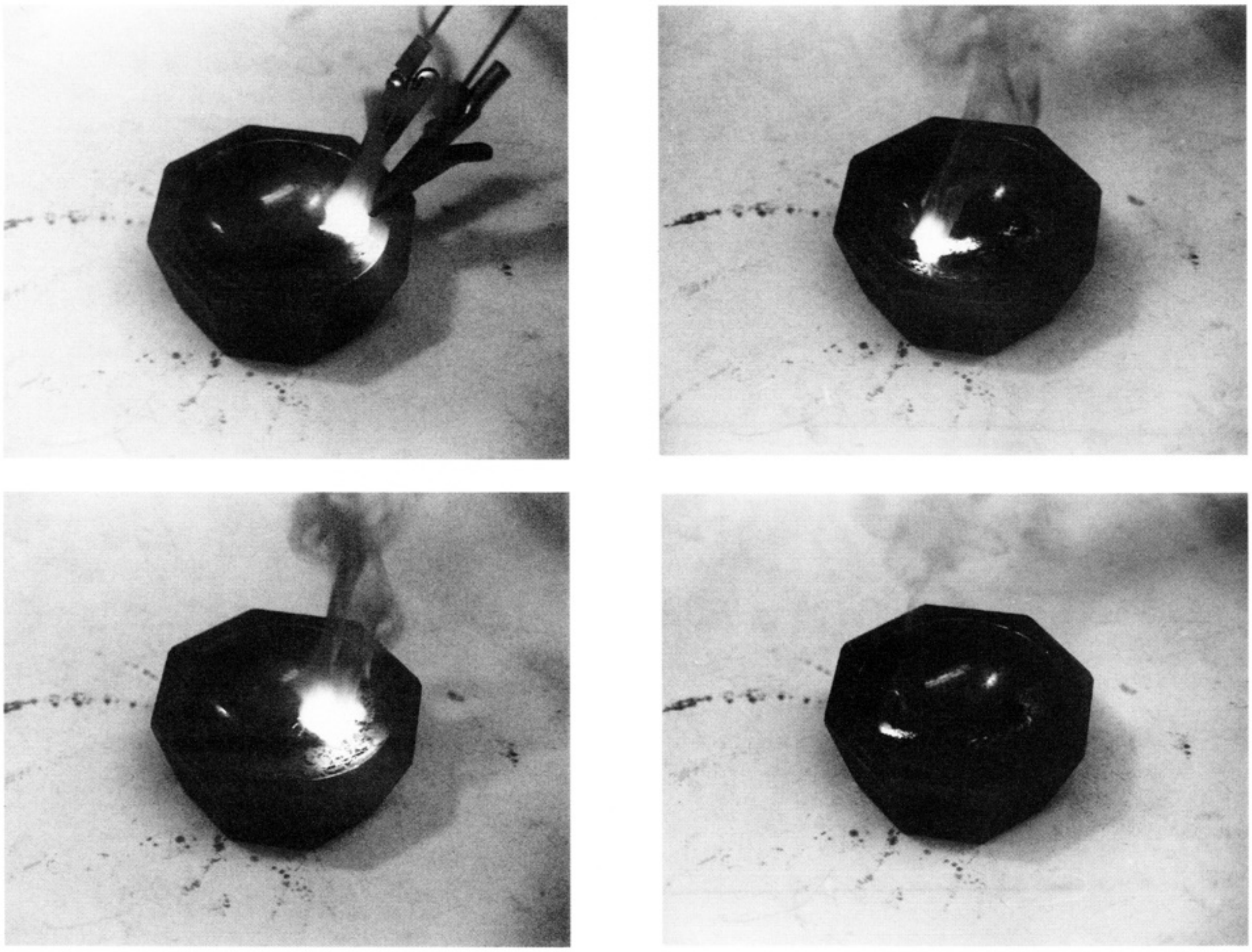

Figure 4. Photographs of the filament-initiated reaction of VCl_3 with a mixture of $1Ca_3N_2{:}2Mg_3N_2$ after (a, top left) 0.7, (b, bottom left) 1.4, (c, top right) 3.5, and (d, bottom right) 4.9 s.

that factors such as particle size, reaction exothermicity, degree of mixing, and melting and vaporization temperatures of components would influence the rate of propagation as has been extensively reported for SHS processes, where propagation velocities from 1 mm s^{-1} to 0.5 m s^{-1} are common.[8]

In some cases, reactions initiated by a hot filament and by thermal initiation in a sealed ampule show some differences in the phases of product observed. It has been found, for example, that filament-initiated reactions of $TiCl_3$ and Li_3N produce TiN and some Ti metal,[17] while the same reaction carried out in a sealed ampule produces only the TiN phase.[16] The reaction of VCl_3 with Mg_3N_2 in a sealed ampule produced VN, while with Ca_3N_2, VN was the major phase with some V_2N also present. Under filament initiation conditions, the magnesium nitride reaction would not propagate but the calcium nitride reaction gave V_2N as the major phase with some VN present. Modifying the nitriding component to a 1:2 mixture of calcium:magnesium nitride allowed the isolation of phase pure V_2N. Thermally initiated reactions in sealed ampules were found to favor more highly nitrided products than the filament-initiated reactions. Modification of the conditions allowed isolation of either vanadium nitride phase at high purity.

Relevance to Reaction Mechanism. The reactions reported herein can be considered to proceed by one of two mechanistic extremes, either reduction to the elements followed by high-temperature recombination (eq 1) or ionic metathesis (eq 2). In many reactions the transition element is reduced, although this does not necessarily rule out the ionic metathesis pathway as the metathesized product could be decomposed by the high reaction temperature (eq 7). For the overall process in

$$HFCl_4 + {}^2/_3Ca_3N_1 \rightarrow {}^1/_3Hf_3N_4 + 2CaCl_2 \rightarrow HfN + {}^1/_2N_2 + 2CaCl_2 \quad (7)$$

eq 7 $\Delta H_r° = -680$ kJ mol^{-1}. Combinations of these two extreme mechanisms may be imagined, where partial decomposition of the chloride releases some chlorine which could then abstract some alkali metal/alkaline earth. The energy so provided could then facilitate a metathetical process.

The reactions of lanthanide chlorides with magnesium or calcium nitride could be promoted only thermally, and the reaction was slow. Uniform heating of the reaction mixture at 550 °C for 1 h produces a mixture of products as identified by XRD, including some metal nitride but largely nitride chlorides, Ca_2NCl and Ln_2Cl_3N. No magnesium nitride chlorides were observed; however, unreacted magnesium nitride was observed in the products after 1 h at 550 °C. Heating the reaction mixture for a longer time diminishes the quantity of nitride chloride and increases the amount of metal nitride, such that for most Ca_3N_2 reactions after 15 h at 550 °C only metal nitride and calcium chloride are observed. The lanthanide chloride reactions, when heated to 900 °C and allowed to cool, produced lanthanide nitride and magnesium or calcium chloride. The observation of intermediates, Ln_2Cl_3N and Ca_2NCl, in the reaction pathway gives strong evidence for an ionic mechanism. No changes in oxidation state are observed in any of the elements, the lanthanide retains the +3 oxidation state from $LnCl_3 \rightarrow Ln_2Cl_3N \rightarrow LnN$. In no cases were the elements observed in the products by XRD, unlike the reactions of magnesium silicide,[15] where this observation was taken to indicate a reductive recombination mechanism.

Kaner and co-workers have recently shown[27] that self-propagation in solid-state metathesis reactions is dependent on the overall reaction enthalpy and crucially on T_{ad}, the adiabatic combustion temperature. For SHS reactions a value of $T_{ad} > 1520$ °C is required for propagation,[8] while in considering SSM reactions to form transition-metal borides $T_{ad,s}$ (the adiabatic combustion temperature for salt formation only, i.e., in the present study this would be calculated for the reaction $Mg_3N_2 + MCl_n \rightarrow MgCl_2 + M + N$) was found to be a more useful parameter and $T_{ad,s} > 740$ °C ensured propagation. This temperature correlated with the temperature required for the salt coproduct $MgCl_2$ to be produced in the liquid phase. Thus self-propagation was found to rely on mediation by the molten salt. If these findings hold for this work then values of $T_{ad,s}$ corresponding to the melting points of $MgCl_2$ and $CaCl_2$ (714 and 782 °C, respectively) would be expected to be important. From Table 3 it is clear that reactions of Ca_3N_2 propagated far more readily than those involving Mg_3N_2. This is due to the difference in exothermicity (eqs 5 and 6). The reactions of VCl_3 self-propagated very quickly with Ca_3N_2 but not at all with Mg_3N_2. A 1:2 mixture of these two reagents led to a reaction which propagated slowly through the reaction mixture, the reaction therefore being only just self-sustaining. The values of $T_{ad,s}$ given in eqs 8–10 explain these data well.

$$VCl_3 + {}^1/_2Mg_3N_2 \rightarrow V + {}^1/_2N_2 + {}^3/_2MgCl_2 \qquad T_{ad,s} = 78\ °C \quad (8)$$

$$VCl_3 + {}^1/_3Mg_3N_2 + {}^1/_6Ca_3N_2 \rightarrow V + {}^1/_2N_2 + MgCl_2 + {}^1/_2CaCl_2 \qquad T_{ad,}3s = 714\ °C \quad (9)$$

$$VCl_3 + {}^1/_2Ca_3N_2 \rightarrow V + {}^1/_2N_2 + {}^3/_2CaCl_2 \qquad T_{ad,s} = 1338\ °C \quad (10)$$

The 1:2 mixture is sufficiently exothermic to melt some of the $MgCl_2$ and allow salt mediation of the reaction. The reactions of $MoCl_5$ and WCl_4 also self-propagate slowly. These reactions are more exothermic than those of Mg_3N_2 with VCl_3 or $TiCl_3$ and in both cases $T_{ad,s}$= 714 °C. For all reactions of the lanthanide chlorides with calcium or magnesium nitride the reactions involving salt formation only are endothermic, so $T_{ad,s}$ is below room temperature, hence the complete lack of propagation in these cases.

Conclusions

The reactions of magnesium and calcium nitride with anhydrous metal chlorides offer a facile route to metal nitrides. The course of the reaction can be determined by the means of initiation, either thermally or by a heated filament. Some control over the propagation wave has been achieved by using a mixture of Ca_3N_2 and Mg_3N_2. The parameter $T_{ad,s}$ is important in determining whether a reaction will self-propagate. $T_{ad,s}$ values of at least the melting point of the group 2 salt product allow propagation. The mechanistic pathway in the lanthanide nitride preparations appears to be via ionic metathesis, as supported by the observation of possible intermediates. Simple one-stage preparations of phase-pure VN and V_2N were reported.

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