# Solid State Metathesis Reactions in Various Applications

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Abstract. Solid state metathesis reactions have been studied in fused silica tubes, by differential thermal analysis, and by X-ray powder diffraction. A selection of reactions between metal (La, Nb, and Ni) chlorides and lithium nitride or lithium acetylide were investigated to get more insight into reaction pathways and intermediate reaction stages that may be adopted on course of the formation of metal nitrides or carbides. Intermediate compounds are considered to be important because they can control the reactivity of a system. Such compounds were traced by changing the molar ratios of reaction partners away from the salt-balanced binary metal nitride or carbide target compositions.

New preparative perspectives are discovered when metal chlorides were reacted with lithium nitridoborate or lithium cyanamide. Due to their reductive nature towards several d-block metal chlorides,  $(BN_2)^{3-}$  and  $(CN_2)^{2-}$  react to form metals or metal nitrides plus X-ray amorphous BN, and probably  $C_3N_4$ . With lanthanum chloride they can react to form nitridoborates and nitridocarbonates. The metathesis reaction between lithium cyanamide and cyanuric chloride  $(C_3N_3Cl_3)$  instead of metal chloride was studied for the synthesis of  $C_3N_4$ .

Keywords: Metathesis reactions; Carbides; Nitrides; Cyanamide; Carbon nitride

# Festkörper-Metathesereaktionen in verschiedenen Anwendungen

Inhaltsübersicht. Festkörper-Metathesereaktionen wurden in zugeschmolzenen Quarzglasampullen, durch Differenz-Thermoanalyse und über Pulver-Röntgenbeugung untersucht. Eine Auswahl von Reaktionen zwischen Metallchloriden (La, Nb und Ni) und Lithiumnitrid oder Lithiumcarbid wurde untersucht, um nähere Aufschlüsse über Reaktionswege und Zwischenstufen bei der Bildung von Metallnitriden und -carbiden zu gewinnen. Intermediär auftretende Verbindungen erscheinen dabei von Bedeutung, weil sie die Reaktivität eines Systems maßgeblich beeinflussen können. Versuche zur Aufspürung solcher Verbindungen wurden unternommen, indem die molaren Verhältnisse der Reaktionspartner von den salzbalancierten Zusammensetzungen, die zur Bildung reiner Metallnitride oder Metallcarbide führen, variiert wurden. Neue präparative Perspektiven eröffnen sich durch Reaktionen von Metallchloriden mit Lithiumnitridoborat oder Lithiumcyanamid. Durch das reduktive Verhalten von  $(BN_2)^{3-}$  und  $(CN_2)^{2-}$  gegenüber 3d-Metallchloriden entstanden bei den Reaktionen elementare Metalle oder Metallnitride plus röntgenamorphes BN und vermutlich  $C_3N_4$ . Mit Lanthanchlorid entstehen Nitridoborate und Nitridocarbonate. Im Zusammenhang mit der Bildung von  $C_3N_4$  wurden Metathesereaktionen untersucht, in denen Cyanurchlorid  $(C_3N_3Cl_3)$  anstatt eines Metallchlorids zur Reaktion mit Lithiumcyanamid eingesetzt wurde.

# Introduction

Syntheses of new solids are often described as explorative or even adventitious rather than on target because the preparative strategies in solid state chemistry are generally not developed far enough. One systematic preparative tool in this widely unexplored field of reaction types are solid state metathesis reactions, typically used in syntheses of refractory nitrides and carbides of d-block elements.

Institut für Anorganische Chemie Universität Tübingen Auf der Morgenstelle 18 D-72076 Tübingen Tel.: 07071-29-76226 Fax: 07071-29-5702 E-mail: juergen.meyer@uni-tuebingen.de Web-Seite: www.uni-tuebingen.de/AK-Meyer A great deal of research on the formation of metal nitrides, carbides, and even borides through solid state metathesis (SSM) reactions has been done by the groups of *Kaner* et al. [1] and *Parkin* et al. [2]. Their reactions often involve a metal (M) halide (X) and an alkaline or alkaline earth (A) main group (Z) compound. If these precursors combine in a highly exothermic solid state metathesis reaction, the reaction ignites at a certain heating temperature and due to its own heat production it quickly propagates through the sample.

Such SSM reactions involve an exchange of ions within the melt of the co-produced salt:

 $MX + AZ \rightarrow [M^+ + Z^- + AX] \rightarrow MZ + AX$ 

Because exothermic reactions can proceed so quickly, it is difficult to monitor local temperatures precisely and to trace reaction pathways. A great amount of heat is produced only for seconds, mainly through the exothermic re-

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lease of lattice energy of the co-produced salt, such as alkaline or alkaline earth halides.

Alternatively, a reductive combination mechanism is considered, in which the metal is fully reduced (M) and the anion is oxidized to its elemental state (Z, e.g. carbon), followed by the reaction of the finely divided elements in a molten flux of the co-produced salt.

 $MX + AZ \rightarrow [M + Z + AX] \rightarrow MZ + AX$ 

The exothermicity of a reaction determines to what extend the propagation of a given reaction occurs. If the heat generation of a reaction is not high enough, further heating is necessary to drive the reaction beyond the elemental state (M + Z) and to produce the desired product. However, intermediate compounds, if existent in these reactions, remain widely unexplored until now.

The goal in our exploration of metathesis reactions was to learn about reaction pathways, possible intermediate compounds, and how to control the reactivity of a system. Our first step was always to perform a salt-balanced reaction to obtain the target composition MZ plus the co-produced salt quantitatively, as shown in the aforementioned model reactions. In order to trace intermediate reaction products, all reactions were scanned by differential thermal analyses, and analysed by X-ray powder diffraction. Reactions were also studied in fused silica tubes being heated at certain temperatures, according to reaction stages indicated by the DTA. As some reactions proceed quickly, a stoichiometric halt was put by changing the relative proportions of reaction partners towards halide-rich compositions, as demonstrated for the reactions between LaCl<sub>3</sub> and Li<sub>3</sub>N with 1:1 and 2:1 molar ratios.

### **Experimental Techniques**

Our experimental conditions involve dry-box technique and reactions in vacuum sealed silica tubes. Commercially available metal halides such as LaCl<sub>3</sub> (Alfa, 99.9%), and NbCl<sub>5</sub> (Strem, 99.99%) were used without further purification. TiCl<sub>3</sub> was prepared from TiCl<sub>4</sub> (Fluka, > 98%) and H<sub>2</sub> (Messer, 5.0) following [3]. NiCl<sub>2</sub> (Strem, > 98%) was sublimed twice under vacuum at 600 °C. Li<sub>3</sub>(BN<sub>2</sub>) was synthesized from Li<sub>3</sub>N (Strem, 99.5%) and dry  $\alpha$ -BN (ABCR, 99.8%) in sealed Ta capsules at 900 °C. Li<sub>2</sub>(CN<sub>2</sub>) was synthesized by heating a mixture of Li<sub>3</sub>N and melamine, C<sub>3</sub>N<sub>3</sub>(NH<sub>2</sub>)<sub>3</sub> (Fluka, > 99%), in an Ar flow slowly up to 650 °C [4]. Li<sub>2</sub>C<sub>2</sub> was synthesized from lithium metal (Strem, 99.99%) and graphite (Alfa, 99.999%) at 850 °C for 24 h in sealed Cu capsules.

Reactions were scanned through differential thermal analyses (Netsch, Simultaneous Thermal Analysis), performed in open Pt or Cu vessels under continuous  $N_2$  flow, or in self-made fused silica ampoule sample holders, using heating rates of 5 °C/minute.

Metathesis reactions were performed separately by heating (fused silica) samples in self-made glass ovens or in commercial furnaces up to different temperatures and durations in order to monitor different reaction stages. All reaction products were characterized by X-ray powder patterns (STOE, STADI-P, Ge monochromated Cu-K<sub> $\alpha$ 1</sub> radiation).

As many solid state reactions are highly exothermic, some starting compounds can react with each other already when being mixed or ground. Examples of spontaneous ignitions (or explosions!) are reactions between NbCl<sub>5</sub> or MoCl<sub>5</sub> and Li<sub>3</sub>N. Caution must be also attended to reactions in which a sudden evolution of gas may burst the ampoule, and also when ampoules with a critical internal pressure are opened through glass-cutting. In order to minimize the risk of an explosion, reactions should be performed on small scale, and in ampoules with sufficient volume.

### The Formation of Metal Nitrides

Metal nitrides can be formed in metathesis reactions between metal chloride and Li<sub>3</sub>N. Metal ions in high oxidation states (+4, +5) are reduced to  $M^{3+}$  under formation of N<sub>2</sub> during the reaction [5].

 $MCl_x + x/3 Li_3N \rightarrow MN + x LiCl + (x-3)/6 N_2$ 

Lithium nitride is a good solid state nitrogen precursor. Due to its thermal stability, it allows to deliver nitrogen in high temperature environments. Several examples of reactions have been studied, and demonstrated this type of solid state metathesis reaction as being very efficient. One example is the formation of rare earth nitrides that are obtained at ignition temperatures around 550 °C under self-sustaining reaction conditions [5, 6].

LaCl<sub>3</sub> and Li<sub>3</sub>N. Reactions between LaCl<sub>3</sub> and Li<sub>3</sub>N were performed in a DTA apparatus by heating the mixture under a continuous flow of N<sub>2</sub>, and in fused silica sample holders, too. An ignition of the 1:1 molar reaction with a strong exothermic formation of LaN was obtained near 500 °C, followed by an endothermic DTA peak near 610 °C, due to the melting of LiCl. The formation of LaN and LiCl was confirmed by X-ray powder patterns.

 $LaCl_3 \,+\, Li_3N \rightarrow LaN \,+\, 3 \,\, LiCl$ 

LaN formed through this route appears as a gray-black powder, indicating the often reported nitrogen deficiency of  $LaN_{1-x}$  samples. A surprisingly high deficiency, with x as big as 0.4 has been reported in a different experiment [6]. If the molar ratio of the reaction partners is changed haliderich,  $La_2NCl_3$  [7] and LiCl are obtained as reaction products, under similar conditions as for LaN.

 $2\ LaCl_3 +\ Li_3N \rightarrow La_2NCl_3 +\ 3\ LiCl$ 

DTA measurements revealed two exothermic signals around 500 °C for the reactions with 1:1 and with 2:1 molar ratios. The signal obtained at lower temperature (495 °C) is stronger in the reaction designed for LaN and the signal obtained at higher temperature (505 °C) is stronger in the reaction designed for La<sub>2</sub>NCl<sub>3</sub> (Fig. 1). The weaker signals obtained could be considered as side-product formations of always the other compound, that is however not detected



**Fig. 1** DTA results of the reaction between  $LaCl_3$  and  $Li_3N$  with a) 1:1 (solid line) and b) 2:1 (dotted line) molar ratios in fused silica tube sample holders (50 mg each, heating rate: 5°C/minute). Two exothermic signals are obtained around 500°C. The signal at lower temperature corresponds to the formation of LaN and the one at higher temperature represents the formation of La<sub>2</sub>NCl<sub>3</sub>.

in the X-ray powder patterns. Still, the formation of La<sub>2</sub>NCl<sub>3</sub> may be easily attributed by small amounts of LaN and vice versa. On the other hand La<sub>2</sub>NCl<sub>3</sub> has been considered as an intermediate compound for the synthesis of LaN [8]. Our results would rather allow an opposite interpretation, because the exothermic effect assigned to the LaN formation is at lower temperature. This assignment was confirmed through a fused silica tube reaction of a 2:1 molar mixture at 480 °C (2 h). The dark-gray product contained mainly LaN, some LiCl, and only little La2NCl<sub>3</sub>. In attempt to suppress the La<sub>2</sub>NCl<sub>3</sub> formation in the synthesis of LaN by stoichiometric means, a halide-deficient experiment was run with 0.9:1 molar ratio. According to our DTA experiment the exothermic effect (at higher temperature) assigned to the formation of La<sub>2</sub>NCl<sub>3</sub> was significantly suppressed.

# The Reduction Case – Oxidation of Nitride and Disproportionation of Acetylide

Lithium nitride as well as lithium acetylide have a reducing nature and can behave very reactive in metathesis reactions. Out of the two types of carbide ions, to be considered as reaction partners in metathesis reactions with a metal chloride, one is C<sup>4-</sup> (as in Al<sub>4</sub>C<sub>3</sub>) and the other is C<sub>2</sub><sup>2-</sup> (as in Li<sub>2</sub>C<sub>2</sub>). In a reductive metathesis reaction C<sub>2</sub><sup>2-</sup> undergoes disproportionation under formation of C<sup>4-</sup> and graphite. Graphite formed in such reactions is difficult to trace because it remains X-ray amorphous if it is not annealed at elevated temperatures.

NbCl<sub>5</sub> and Li<sub>3</sub>N. The reaction between niobium pentachloride and lithium nitride has been described to yield cubic NbN (NaCl type structure) plus the nitrogendeficient hexagonal  $\beta$ -Nb<sub>2</sub>N phase as a side-product, after



Fig. 2 Powder XRD results obtained from the reaction of  $NbCl_5$  with  $Li_3N$  after spontaneous ignition and following treatment at 250 °C. Circles indicate LiCl, and crosses represent  $Li_7NbN_4$ .

ignition with a nichrome wire at 850 °C in a stainless steel reactor [8].

NbCl<sub>5</sub> + 5/3 Li<sub>3</sub>N  $\rightarrow$  NbN + 5 LiCl + 1/3 N<sub>2</sub>

It should be noted, however, that the reaction between niobium pentachloride and lithium nitride ignites spontaneously (explosion with production of light and heat) when being ground at room temperature. Therefore, our experiments were simply performed in a dry box under nitrogen using an agate mortar (with up to 200 mg NbCl<sub>5</sub>). On grinding mixtures of the same molar ratio as in the aforementioned synthesis of NbN, we obtained Li<sub>7</sub>NbN<sub>4</sub> [9] and LiCl as main products. This result was confirmed after grinding a reaction mixture, composed for the synthesis of Li<sub>7</sub>NbN<sub>4</sub>:

 $NbCl_5 + 4 \ Li_3N \rightarrow Li_7NbN_4 + 5 \ LiCl$ 

Besides  $Li_7NbN_4$  and LiCl, only small amounts of  $Li_3N$  and  $Li_9Cl_3N_2$  where obtained as side products, which almost disappeared when the sample was annealed for one day at 250 °C (Fig. 2). This synthetic route for  $Li_7NbN_4$  is surprisingly easy, especially when compared with the original solid state synthesis from niobium,  $Li_3N$  and nitrogen in an autoclave reaction at 770 °C [19].

Because  $Li_7NbN_4$  with  $Nb^{5+}$  was not considered as a precursor for NbN, an alternative pathway of the reaction was desired. In attempt to slow the reaction rate of this strongly exothermic formation reaction down, three different experiments with 1:4 molar ratios were launched:

1. The NbCl<sub>5</sub>/Li<sub>3</sub>N mixture was diluted with different amounts of LiCl. When NbCl<sub>5</sub> was mixed with 4 mole of LiCl, and afterwards strongly ground with Li<sub>3</sub>N, a slow reaction yielded a complete consumption of NbCl<sub>5</sub>. The Xray powder pattern showed LiCl, very little Li<sub>3</sub>N, and reflections of an unknown compound (called: phase A1), which transforms into poorly crystalline niobium nitrides



Fig. 3 Powder XRD results obtained from the (2:5) reaction of NbCl<sub>5</sub> with  $Li_2C_2$  at 400 °C (bottom), and 600 °C (top). In the reaction at 600 °C LiCl was separated from the reaction product. Circles indicate reflections of LiCl, bars niobium, and squares represent Nb<sub>6</sub>C<sub>5</sub>.

(mostly  $Nb_4N_3$ ) when the product mixture was heated above 300 °C.

2. Another slow reaction was prepared in a fused silica tube, in which both reaction partners were separated from each other. When the ampoule was heated at 300 °C solid  $Li_3N$  was exposed with NbCl<sub>5</sub> vapor. The powder pattern of the product revealed LiCl together with the unknown pattern similar to that of phase A1. Since this phase occurs dark gray or black and the ampoule was under (supposed N<sub>2</sub>) pressure, we concluded that a redox reaction between Nb<sup>5+</sup> and N<sup>3-</sup> has taken place.

3. A similar reaction product as before was obtained when small portions of  $Li_3N$  (about 10 mg) are ground step by step into (about 200 mg) finely divided NbCl<sub>5</sub> powder.

NbCl<sub>5</sub> and Li<sub>2</sub>C<sub>2</sub>. The synthesis of Nb<sub>6</sub>C<sub>5</sub> was studied by reactions between niobium pentachloride and lithium ace-tylide following a salt-balanced stoichiometry.

2 NbCl<sub>5</sub> + 5 Li<sub>2</sub>C<sub>2</sub>  $\rightarrow$  1/3 Nb<sub>6</sub>C<sub>5</sub> + 10 LiCl + 25/3 C

This reaction, however, is not nearly as efficient as the previous reaction with lithium nitride. External heating is necessary to drive the reaction to completeness. On heating the reaction mixture (fused ampoule) in a DTA apparatus several exothermic effects (about three between 150 and  $320 \,^{\circ}$ C, and one near  $580 \,^{\circ}$ C) were monitored, without detecting the melting point of NbCl<sub>5</sub> (near 200  $\,^{\circ}$ C). From reactions performed in fused silica tubes at 400  $\,^{\circ}$ C (10 h) a complete reduction of all Nb<sup>5+</sup> into niobium metal was obtained in X-ray powder patterns. If the reaction temperature was raised to 600  $\,^{\circ}$ C (10 h) Nb<sub>6</sub>C<sub>5</sub> develops as the main product, according to the X-ray powder pattern (Fig. 3).

In following reactions the molar ratio of the starting materials was varied towards halide-rich in order to get some idea about possible intermediate products along the way on stepwise reduction of  $Nb^{5+}$  in  $NbCl_5$ .

The equimolar reaction between niobium pentachloride and lithium acetylide was considered capable for the reductive synthesis of  $LiNb_6Cl_{19}$  [11], containing trigonal ni-



**Fig. 4** Powder XRD patterns obtained from the (1:1) reaction of NbCl<sub>5</sub> with Li<sub>2</sub>C<sub>2</sub> at 160 °C (bottom), 270 °C (middle), and 600 °C (top). Reflections of LiCl are marked with circles, NbCl<sub>4</sub> with squares, and the A phase with triangles. Reflections of the sample holder are marked with asterisks.

obium clusters. This compound, originally synthesized by a three powder process from NbCl<sub>5</sub>, Nb metal, and  $Li_2C_2$  (in 4:2:0.5 molar ratio) at 500 °C was, however, not obtained through the attempted two powder route:

"6 NbCl<sub>5</sub> + 6 Li<sub>2</sub>C<sub>2</sub>  $\rightarrow$  LiNb<sub>6</sub>Cl<sub>19</sub> + 11 LiCl + 12 C"

When the reaction mixture was heated (sealed tube) in a DTA apparatus, several thermal effects occurred in the temperature range between 150 and 300 °C. A clear identification of the X-ray powder patterns from samples reacted at low temperatures remains tackling. The pattern at 160 °C can be compared with a slightly shifted pattern of NbCl<sub>4</sub> [12]. The formation of LiCl can be identified in the X-ray powder pattern of samples reacted up to 270 °C together with an unidentified product, with a pattern related, but being slightly shifted in  $2\theta$  when compared with that of the previously mentioned phase A1. When the reaction mixture was annealed in fused silica tubes to 600 °C for two days, an X-ray powder pattern related to that of Nb<sub>3</sub>Cl<sub>8</sub> [13, 14] was obtained together with lines of LiCl (Fig. 4). The identification of this product next to LiCl is however not safe, due to the few number of lines obtained in the pattern.

6 NbCl<sub>5</sub> + 7 Li<sub>2</sub>C<sub>2</sub>  $\rightarrow$  2 Nb<sub>3</sub>Cl<sub>8</sub> + 14 LiCl + 14 C

If the amount of niobium chloride in the reaction is further increased, NbCl<sub>4</sub> plus LiCl are identified as reaction products in fused silica tube reactions after two days at  $160 \,^{\circ}\text{C}$  according to X-ray powder patterns. At lower reaction temperatures an X-ray powder pattern corresponding to a new phase A2 was obtained (Fig. 5).

 $NbCl_5 + 1/2 Li_2C_2 \rightarrow NbCl_4 + LiCl + C$ 

**NbCl<sub>5</sub> and LiH.** Niobium pentachloride was reacted with lithium hydride at 70 °C, 12 h under vacuum, or under flowing Ar (Fig. 6). In a related experiment niobium pentachloride was reacted with lithium metal in a fused silica tube at



**Fig. 5** Powder XRD patterns of the (2:1) reaction of NbCl<sub>5</sub> with  $\text{Li}_2\text{C}_2$  at 80 °C (bottom), and 160 °C (top). Reflections of LiCl are marked as circles, and the strongest ones of NbCl<sub>4</sub> with squares. All remaining reflections in the pattern at 160 °C with I < 10% (I<sub>max.</sub>) belong to NbCl<sub>4</sub>. Phase A2 is represented by triangles and reflections from the sample holder are marked with asterisks.



**Fig. 6** Powder XRD patterns of the (1:1) reaction of NbCl<sub>5</sub> with LiH yielding phase A2 (triangles) at 80 °C (bottom), and yielding NbCl<sub>4</sub> (filled squares) plus LiCl (circles) at 220 °C (top). For NbCl<sub>4</sub> only reflections with  $I/I_{max.} > 10\%$  are marked. One reflection (open square) is considered as NbOCl<sub>3</sub>. Reflections from the sample holder are marked with asterisks.

90 °C for 4 weeks. The X-ray powder patterns of all reaction products were closely related, exhibiting one strong reflection near  $2\Theta = 15^{\circ}$ , corresponding with phase A2, and no lines of LiCl. If the reaction temperature is raised, the formation of LiCl is obtained. At 220 °C NbCl<sub>4</sub> and LiCl can be identified from the powder patterns (Fig. 6). Electrochemical Li intercalations into NbCl<sub>5</sub> have suggested a reversible intercalation for Li<sub>x</sub>NbCl<sub>5</sub> with 0 < x < 0.75 [15]. However, a chemical reaction between LiCl and NbCl<sub>4</sub> remains unknown.

NbCl<sub>5</sub> + LiH  $\rightarrow$  phase A2 +  $^{1}/_{2}$  H<sub>2</sub>

With a flow of hydrocarbon, such as hexane, phase A2 readily reacts to form niobium carbide near  $350 \,^{\circ}$ C. In fact the reaction can be also performed in one step from NbCl<sub>5</sub> and LiH under flowing hexane to yield Nb<sub>6</sub>C<sub>5</sub> at surprisingly low reaction temperatures desired for the synthesis of carbide materials.

 $NbCl_5 + LiH + 5/6 C_6H_{14} \rightarrow 1/6 Nb_6C_5 + LiCl + volatile products$ 

The intermediate phase A2 is likely to be a compound in the system Li-Nb-Cl. With Nb<sup>5+</sup> only LiNbCl<sub>6</sub> has been reported to exist between 206 and 257 °C or 190 and 251 °C, respectively [16]. This phase is however different from our phase A2 which decomposes to yield LiCl and NbCl<sub>4</sub> as the only crystalline products detectable in the X-ray powder patterns. A compound in the system Li-Nb-Cl with tetravalent niobium is still unknown. Only LiNb<sub>6</sub>Cl<sub>19</sub> and Nb<sub>3</sub>Cl<sub>8</sub> [14] have been reported as host structures for lithium.

NiCl<sub>2</sub> and Li<sub>3</sub>N. Nickel chloride reacts with Li<sub>3</sub>N to form nickel metal, LiCl, plus nitrogen.

NiCl<sub>2</sub> + 2/3 Li<sub>3</sub>N  $\rightarrow$  Ni + 2 LiCl + 1/3 N<sub>2</sub>

The formation of metal powder from this type of reaction has been reported for reactions of several metal chlorides of d block elements (M = Mo, W, Fe, Co, Ni, Cu, Pt, Zn, Cd) with Li<sub>3</sub>N [17]. An inspection of the reaction between nickel chloride and lithium nitride by DTA analyses shows an exothermic effect near 450 °C. No formation of Ni<sub>3</sub>N is obtained, that is essentially stable between 350 °C and 500 °C [18].

### Reactions with $Li_3(BN_2)$ and $Li_2(CN_2)$

In order to develop metathesis reactions towards different preparative perspectives it appears interesting to look at reactions in which  $Li_3(BN_2)$  or  $Li_2(CN_2)$  are employed instead of lithium nitride or carbide. Both compounds alone can be heated in Ta ampoules up to temperatures as high as 800 °C without decomposition. In combination with metal halides, however, they behave reactive at lower temperatures.

LaCl<sub>3</sub> and Li<sub>3</sub>(BN<sub>2</sub>). The synthesis of lanthanum nitridoborate via solid state metathesis reaction between lanthanum trichloride and lithium nitridoborate has been reported recently [19]. This reaction occurs at a significantly lower reaction temperature than the straight-forward synthesis starting from LaN and hexagonal BN.

 $LaCl_3 + Li_3(BN_2) \rightarrow La(BN_2) + 3 LiCl$ 

According to DTA measurements a single exothermic effect is obtained near 580 °C.  $La(BN_2)$  formed in this reaction is better expressed as  $La_3(B_3N_6)$ , due to the trimerization of  $(NBN)^{3-}$  units, delivered by  $Li_3(BN_2)$ , during the reaction. The poorly crystalline lanthanum nitridoborate can be crystallized from the co-produced LiCl flux by annealing. Several nitridoborate nitrides can be obtained through the same route when  $Li_3N$  is included into the metathesis reaction [20].

 $TiCl_3$  and  $Li_3(BN_2)$ . With d-block elements no nitridoborates are known. Reactions between equimolar ratios of titanium trichloride and lithium nitridoborate were performed in fused silica tubes.

$$TiCl_3 + Li_3(BN_2) \rightarrow TiN + 3 LiCl + BN$$



Fig. 7 Powder XRD pattern of reaction products of the reaction between NbCl<sub>5</sub> with Li<sub>3</sub>(BN<sub>2</sub>) after annealing at 850 °C (bottom) and at 1050 °C (top). Crosses represent cubic NbN, open circles represent  $\epsilon$ -NbN, and filled circles represent the formation of  $\delta$ -NbN. The 002 reflection of hexagonal BN is at  $2\Theta = 26.7^{\circ}$ .

If the starting mixture is heated in a DTA apparatus, TiN is formed in a strongly exothermic reaction at 580 °C. The X-ray powder patterns showed broad lines of TiN plus lines of well crystalline LiCl. The occurrence of BN in the reaction product is without proof.

NbCl<sub>5</sub> and Li<sub>3</sub>(BN<sub>2</sub>). Niobium pentachloride reacts with lithium nitridoborate to form niobium nitrides. According to X-ray powder pattern taken at successive reaction stages performed in fused silica tubes, broad reflections of some niobium nitrides can be obtained at 300 °C together with reflections of LiCl.

3 NbCl<sub>5</sub> + 5 Li<sub>3</sub>(BN<sub>2</sub>)  $\rightarrow$  3 NbN + 15 LiCl + 5 BN + N<sub>2</sub>

In order to clearly determine the identity of the nitrides, the samples were annealed in fused silica tubes at 850 and 1050 °C for 10 hours, and X-ray powder pattern were taken as shown in Fig. 7, after removing LiCl by washing with water. The main product annealed at 850 °C was cubic NbN (Fm3m, NaCl type) with a = 436.3(3) pm. After treatment at 1050 °C  $\epsilon$ -NbN (P6<sub>3</sub>/mmc, AABB stacking derivative, TiP type) was obtained with lattice parameters a = 296.00(4) and c = 1126.4(2) pm. From both patterns, smaller fractions ( $\approx$  15%) of  $\delta$ -NbN (P6<sub>3</sub>/mmc, anti-NiAs type) and the 002 reflection of hexagonal BN at 2 $\Theta$  = 26.7° were observed.

 $NiCl_2$  and  $Li_3(BN_2)$ . In the reaction with nickel chloride, nickel is fully reduced to its elemental state in one exothermic step near 600 °C.

 $NiCl_2 + 2/3 Li_3(BN_2) \rightarrow Ni + 2 LiCl + 2/3 BN + 1/3 N_2$ 

The X-ray powder pattern of the product shows LiCl and Ni only (Fig. 8). The presence of X-ray amorphous BN in the reaction product was approved by three methods: (1) by



Fig. 8 Powder XRD results obtained from the reaction of  $NiCl_2$  with  $Li_3(BN_2)$  at 600 °C. Circles indicate LiCl, and bars reflections of Ni.

an infrared spectrum taken from the reaction product (KBr pellet), (2) by re-annealing amorphous BN, and (3) by chemical reaction of amorphous BN.

An infrared spectrum of the reaction product exhibited a pattern typical for hexagonal BN. For the following two experiments the reaction product was washed with diluted nitric acid and a white residue was filtered off. This residue was heated in a sealed tantalum ampoule at  $1250 \,^{\circ}$ C. The X-ray powder pattern of the annealed product revealed reflections of hexagonal BN only. In the third experiment the white residue (after washing) was dried in air at  $100 \,^{\circ}$ C for two hours. Afterwards it was weighted (assuming the mass of BN) to react with an equimolar amount of Li<sub>3</sub>N in a sealed copper tube at 800  $^{\circ}$ C. The product was at least 85% clean Li<sub>3</sub>(BN<sub>2</sub>).

LaCl<sub>3</sub> and Li<sub>2</sub>(CN<sub>2</sub>). The synthesis of the unknown compound "La<sub>2</sub>(CN<sub>2</sub>)<sub>3</sub>" was attempted through the salt-balanced metathesis reaction between lanthanum chloride and lithium cyanamide in sealed Ta ampoules.

2 LaCl<sub>3</sub> + 3 Li<sub>2</sub>(CN<sub>2</sub>) 
$$\rightarrow$$
 La<sub>2</sub>Cl(CN<sub>2</sub>)N + 5 LiCl + 1/3 Li<sub>3</sub>N + 2/3 C<sub>3</sub>N<sub>4</sub>

At 850 °C the new compound La<sub>2</sub>Cl(CN<sub>2</sub>)N [21] was obtained together with LiCl according to X-ray powder patterns. The formation of a nitride from a cyanamide in this reaction was not clearly understood at this stage, and the formation of  $C_3N_4$  was only assumed. A stoichiometric reaction for the synthesis of La<sub>2</sub>Cl(CN<sub>2</sub>)N was afterwards performed with lithium nitride at 750 °C. Only the desired La<sub>2</sub>Cl(CN<sub>2</sub>)N (a = 1337.7(4) pm, b = 961.9(2) pm, c = 395.24(9) pm, from orthorhombic indexing of 30 lines) plus LiCl were obtained from X-ray powder patterns (Fig. 9).

 $2\ LaCl_3 +\ Li_2(CN_2) +\ Li_3N \rightarrow La_2Cl(CN_2)N +\ 5\ LiCl$ 

Due to the presence of  $Li_3N$  in this reaction the intermediately formed  $La_2NCl_3$  can control the reactivity of the sys-



Fig. 9 Powder XRD pattern of  $La_2Cl(CN_2)N$  (top) together with lines of the calculated pattern (bottom). Circles indicate LiCl.

tem away from the cyanamide towards cyanamide nitride. Therefore, the reaction between  $La_2NCl_3$  and  $Li_2(CN_2)$  performs easily, too (at 750 °C).

In spite of the plausible explanation on the formation of  $La_2Cl(CN_2)N$ , the 2:3 molar reaction between lanthanum trichloride and lithium cyanamide raises questions regarding some side products. As shown previously, metal halides can react with  $(C_2)^{2-}$  or  $(BN_2)^{3-}$  to form metal carbide or nitride plus graphite or BN. In the case of  $(CN_2)^{2-}$  we may also consider a disproportionation into nitride ions plus formation of neutral carbon nitride. What we have considered as  $C_3N_4$  in the first reaction is obtained as a brown powder that decomposes above 600 °C to yield volatile products according to DTA measurements.

NiCl<sub>2</sub> and Li<sub>2</sub>(CN<sub>2</sub>). From the reaction between NiCl<sub>2</sub> and lithium cyanamide at 500 °C only reflections of Ni and LiCl were obtained in the X-ray powder pattern. However the reaction is much more complicated. As in the former reaction with LaCl<sub>3</sub>, a brown residue was obtained in the reaction product that is supposed to be X-ray amorphous carbon nitride.

 $NiCl_2 + Li_2(CN_2) \rightarrow Ni + 2 LiCl + 1/3 C_3N_4 + 1/2 N_2$ 

The DTA measurement of the reaction (fused silica tube) shows several relatively broad exothermic effects (at least five) between 300 and 500 °C. According to the powder pattern taken from products at different temperatures, the formation of intermediate  $Ni_3N$  begins at 300 °C. At 500 °C  $Ni_3N$  is fully decomposed into Ni metal (and  $N_2$ ). In this temperature interval there are some shifts of reflections of the  $Ni_3N$  structure towards increasing lattice parameters. These shifts could be due to a steady incorporation of nitrogen, but maybe carbon, too ( $Ni_3(N,C)$ ).

# Reactions of $C_3N_3Cl_3$ with $Li_2(CN_2)$ – The $C_3N_4$ Problem

The concept of metathesis reactions has been already used as a strategy for the synthesis of several interesting materi-



Fig. 10 DTA of the reaction between cyanuric chloride and  $Li_2(CN_2)$  (2:3 molar ratio) in a fused silica tube sample holder (heating rate: 5 °C/minute).

als. The synthesis of carbon nanotubes has been performed by solid state conproportionation metathesis reaction of the differently charged carbons in hexachloroethane and in lithium acetylide [22]. Cubic boron nitride was synthesized under low-pressure and low-temperature conditions from a solution (benzene) metathesis reaction between BBr<sub>3</sub> and Li<sub>3</sub>N in an autoclave [23]. In addition a new carbon nitride (C<sub>3</sub>N<sub>4</sub>) synthesis has been reported recently from the solid state reaction of C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> with Li<sub>3</sub>N [24]. We have considered a similar preparative strategy in our reaction of C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> with Li<sub>2</sub>(CN<sub>2</sub>).

 $2/3 \text{ } \mathrm{C_3N_3Cl_3} + \text{Li}_2(\text{CN}_2) \rightarrow \text{C}_3\text{N}_4 + 2 \text{ } \text{LiCl}$ 

The DTA measurement of this reaction in a fused silica tube shows an endothermic effect near 150 °C, consistent with melting point of cyanuric chloride (at 154 °C). An exothermic reaction is obtained near 500 °C (Fig. 10). However the X-ray powder patterns of the product shows only crystalline LiCl. After LiCl is washed off with water the remaining brown powder was again studied by DTA. An exothermic decomposition of  $C_3N_4$  occurs between 600 and 700 °C (under N<sub>2</sub>).

Carbon nitride materials, synthesized through several preparative routes are generally not well characterized as they occur X-ray amorphous, and are, due to the lack of high quality data, even hard to compare.

## **Summary and Conclusion**

In solid state metathesis reactions some critical temperature is required to overcome the solid state diffusion barrier and to allow a reaction to spread through the sample. For the propagation of the reaction throughout the whole sample it is important that an exothermic effect, provided in part by the lattice energy of the co-produced salt, is driving the reaction towards completeness, or that appropriate external heating provides sufficient energy. Efficient examples of

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SSM are reactions exhibiting one strongly exothermic step, as seen for the formations of  $La_2NCl_3$ , LaN,  $Li_7NbN_4$ , TiN, and  $La_3B_3N_6$  in which sufficient energy is provided internally to drive reactions to completeness.

Depending on the reaction pathway, a reaction may involve several exothermic and endothermic partial reactions that can speed the reaction up or slow it down. Therefore the stability of intermediate compounds is important for the efficiency of a reaction. If a reaction is not exothermic enough, it remains incomplete until external heating will serve to completeness. In case of our Nb<sub>6</sub>C<sub>5</sub> formation the metathesis reaction passes several not well analyzed stages and through the elemental state of niobium, before the reaction with finely divided carbon leads to Nb<sub>6</sub>C<sub>5</sub>. The example shown for the synthesis of Nb<sub>6</sub>C<sub>5</sub> suggests simultaneous diffusion of Li<sup>+</sup> into metal chloride (NbCl<sub>5</sub>) and reduction of Nb<sup>5+</sup> by carbide as one possible mechanism for the initiation of the metathesis reaction.

After the development of a metathesis route for the synthesis of lanthanum nitridoborate(nitride)s from LaCl<sub>3</sub> and Li<sub>3</sub>(BN<sub>2</sub>) (plus Li<sub>3</sub>N), it was shown for the first time that a nitridocarbonate nitride can be formed in analogous metathesis reactions with Li<sub>2</sub>(CN<sub>2</sub>) (plus Li<sub>3</sub>N).

Reactions of lithium nitridoborate and cyanamide with some d-block metal halides lead to the breakdown of the triatomic anions, yielding amorphous BN and probably  $C_3N_4$ :

 $(BN_2)^{3-} \rightarrow BN + N^{3-}$ 3  $(CN_2)^{2-} \rightarrow C_3N_4 + 2 N^{3-}$ 

In these reactions the nitride ions may combine with the metal to form nitrides, as for the case of TiN and NbN, or reduce the metal to its elemental state to form nitrogen, as in the case of Ni (and several other d-block elements). A definite identification of  $C_3N_4$  is however difficult, especially due to its limited thermal stability. X-ray amorphous  $C_3N_4$  samples obtained from our experiments exhibited analogous decomposition temperatures as other samples of this type obtained from different reactions. Still this type of materials is not well enough defined. Our preparative approach of a metathesis between cyanuric chloride and lithium cyanamide has yielded interesting  $C_3N_4$  materials, sometimes forming some brown needles, when performed under clean and well designed conditions.

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