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(54) Titre : PROCEDE DE PRODUCTION D'HALOGENURES DE METAUX TERREUX RARES ANHYDRES, DE MELANGES DE SYNTHESE CONTENANT DES HALOGENURES DE METAUX TERREUX RARES ANHYDRES ET LEUR UTILISATION

(54) Title: METHOD FOR THE PRODUCTION OF WATER-FREE RARE EARTH METAL HALOGENIDES, SYNTHESIS MIXTURES CONTAINING WATER-FREE RARE EARTH METAL HALOGENIDES AND USE THEREOF

(57) Abrégé/Abstract:
The invention relates to a method wherein rare earth metal oxides are reacted with halogenation agents of general formula (1), wherein M= Si, Ge, Sn, Ti, Zr, Hf; Hal= Cl, Br, I; X^1,X^2,X^3 = independently from each other Cl, Br, I, H, alkoxy (-OR), wherein R represents an organo radical having 1-20 atoms, alkyl having 1-20 C atoms or aryl with 6-20 C atoms, wherein the alkyl or arly radicals can include one or several halogen substituents selected from the group of F, Cl, Br or I; in an aprotic polar solvent. The invention also relates to synthesis mixtures containing water-free rare earth metal halogenides and the use thereof

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(54) Title: METHOD FOR THE PRODUCTION OF WATER-FREE RARE EARTH METAL HALOGENIDES, SYNTHESIS MIXTURES CONTAINING WATER-FREE RARE EARTH METAL HALOGENIDES AND USE THEREOF

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON WASSERFREIEN SELTENERDMETALLHALOGENIDEN, WASSERFREIE SELTENERDMETALLHALOGENIDE ENTHALTENDE SYNTHESEGEMISCHE UND DEREN VERWENDUNG

(57) Abstract: The invention relates to a method wherein rare earth metal oxides are reacted with halogenation agents of general formula (1), wherein M= Si, Ge, Sn, Ti, Zr, Hf; Hal= CI, Br, I; X^1,X^2,X^3 = independently from each other CI, Br, I, H, alkoxy (-OR), wherein R represents an organo radical having 1-20 atoms, alkyl having 1-20 C atoms or aryl with 6-20 C atoms, wherein the alkyl or arly radicals can include one or several halogen substituents selected from the group of F, CI, Br or I; in an aprotic polar solvent. The invention also relates to synthesis mixtures containing water-free rare earth metal halogenides and the use thereof

(57) Zusammenfassung: Beschrieben wird ein Verfahren, bei dem Seltenerdmetalloxide mit Halogenierungsmitteln der allgemeinen Formel: $MHalX^1X^2X^3$ (1) mit M = Si, Ge, Sn, Ti, Zr, Hf; Hal = Cl, Br, I; X^1, X^2, X^3 = unabhängig voneinander Cl, Br, I, H, Alkoxy (-OR), wobei R einen Organorest mit 1 - 20 C-Atomen darstellt, Alkyl mit 1 bis 20 C Atomen oder Aryl mit 6 bis 20 C-Atomen, wobei die Alkyl- oder Arylreste einen oder mehrere weitere Halogensubstituenten, ausgewählt aus der Gruppe F, Cl, Br oder I, tragen können in einem aprotischen, polaren Lösemittel umgesetzt werden. Beschrieben werden ferner wasserfreie Seltenerdmetallhalogenide enthaltende Synthesegemische und deren Verwendung.

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METHOD FOR THE PRODUCTION OF WATER-FREE RARE EARTH METAL HALOGENIDES, SYNTHESIS MIXTURES CONTAINING WATER-FREE RARE EARTH METAL HALOGENIDES AND USE THEREOF

The invention relates to a method for the production of anhydrous rare-earth metal halides, synthesis mixtures containing anhydrous rare-earth metal halides and the use thereof.

Rare-earth metal halides ($REHal_3$ where RE = scandium, yttrium, lanthanum and lanthanoids (Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and Hal = Cl, Br or I) are used in anhydrous form as reagents in organic synthesis or they serve as starting compounds for the production of further rare-earth compounds such as rare-earth alkoxides or rare-earth organyls. For example, starting from the THF complex of neodymium chloride, allyl neodymium compounds are produced which find use as catalysts for stereospecific butadiene polymerisation (EP 919 573, R. Taube et al., *J. Organomet. Chem.* 1 (513), 37-47, 1996).

Rare-earth metal halides are produced most easily by reacting the oxides with aqueous acids. Solutions of the rare-earth metal halides are obtained in this way, from which the halide salts can be obtained in the form of their crystalline aquo complexes by cooling and/or evaporation. The anhydrous halides *cannot* be obtained directly from these hydrates, however, as they give off hydrogen halide as well as water when heated and are converted into oxygen-containing solids such as halide oxides or even the pure oxides (this applies to $(ScCl_3)_{aq}$ for example):

$$RE_2O_3 + 6\,HHal \xrightarrow{H_2O} 2\,(REHal_3)_{aq} \xrightarrow[-H_2O,-HHal]{} {}^{\Delta T}\ REOHal$$

Only under very gentle conditions and in a few cases can anhydrous halides be prepared from the hydrates under purely physical drying conditions. To this end the hydrate compound must first be heated under a stream of hydrogen halide gas (HHal) whilst following a precise temperature regime. For example, anhydrous $NdCl_3$ is obtained by holding $NdCl_3 \cdot 6\ H_2O$ under reduced pressure in an HCl atmosphere, initially at 80°C until most of the water has been driven off, then at 160°C for 2 to 3 hours and finally at 250°C. The HCl is then replaced by dry nitrogen and cooled. After dehydration the product, which still contains residual oxygen, is purified by vacuum sublimation at 1000 K (Gmelins Handbook of Inorg. Chem., 8th ed., Sc, Y, La-Lu, Part C4b, p. 156). The disadvantages of this method are the expensive apparatus (resistance to corrosion at high temperatures), the complex process per se and the long synthesis times.

For that reason alternative production methods have been developed, which are described briefly below.

Anhydrous chlorides can be prepared by heating the oxides or carboxylic acid salts (e.g. the oxalates) with ammonium chloride:

$$RE_2O_3 + 6\ NH_4Cl \xrightarrow{\text{approx. } 300°C} 2\ RECl_3 + 3\ H_2O \uparrow + 6\ NH_3 \uparrow$$

The disadvantages are the high temperatures and the formation of a gaseous, corrosive by-product (NH_3).

Instead of ammonium chloride, other chlorinating agents such as S_2Cl_2 or Cl_2/S_2Cl_2 mixtures can also be used. In this case too, the synthesis as follows

$$4\ RE_2O_3 + 3\ S_2Cl_2 + 9\ Cl_2 \rightarrow 8\ RECl_3 + 6\ SO_2 \uparrow$$

requires high temperatures (500 to 1000°C) and a toxic, corrosive by-product is formed. $SOCl_2$ can also be used in a similar way (Gmelin C4a, p. 56-58).

Tetrachloromethane and CCl_4/Cl_2 mixtures are also capable of chlorinating rare-earth metal oxides at high temperatures:

$$RE_2O_3 + 3\ CCl_4 \rightarrow 2\ RECl_3 + 3\ Cl_2 \uparrow + 3\ CO \uparrow$$

$$RE_2O_3 + 3\ CCl_4 \rightarrow 2\ RECl_3 + 3\ COCl_2 \uparrow$$

As with the synthesis variants mentioned above, high temperatures (500 to 700°C) are required and undesirable by-products form (Gmelin C4a, 58-59). The same is also true of the other known chlorinating agents, namely PCl_5 and amine hydrochlorides (Gmelin C4a, p. 59-60).

An object of the present invention is to present a method for producing anhydrous rare-earth metal halides $REHal_3$ which avoids the disadvantages of the methods known hitherto and in particular yields the anhydrous halide salts $REHal_3$ directly from the rare-earth metal oxides under gentle reaction conditions (in other words under normal pressure and at ≤ approx. 150°C) and without the formation of corrosive or toxic by-products.

More particularly, the object is achieved a method for producing anhydrous rare-earth metal halides ($REHal_3$), comprising reacting a rare-earth metal oxide of the formula RE_2O_3, wherein RE is Sc, Y, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, with a halogenating agent of the formula (1);

$$MHalX^1X^2X^3 \quad (1)$$

Wherein: M is Si, Ge, Sn, Ti, Zr or Hf;

Hal is Cl, Br or I; and

X1, X2 are X3 are each independently Cl, Br, I, H, alkoxide -OR wherein R is an organic radical having 1-20 C atoms, an alkyl having 1-20 C atoms or an aryl having 6-20 C atoms, wherein the alkyl or aryl radicals can be substituted at least once with F, Cl, Br or I;

in one or more of an aprotic, polar solvent.

The invention is also directed to the use of a reaction mixture comprising a rare-earth oxide of formula RE_2O_3, a halogenating agent and a polar, aprotic solvent or an aprotic solvent blend, as a reagent or catalyst in an organic or inorganic reaction, wherein

RE is selected from the group consisting Sc, Y, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

the halogenating agent is selected from the group consisting of $SiCl_4$, $SiBr_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $TiBr_4$, $C_6H_5SiCl_3$, 4-$ClC_6H_4SiCl_3$, 4-$BrC_6H_4SiCl_3$, $HSiCl_3$, $(H_3C)_2ClSiCH_2Cl$, $(H_3C)_2ClSiCH_2Br$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$; and

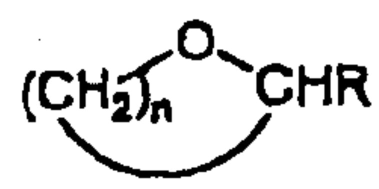
the polar, aprotic solvent or the aprotic solvent blend is selected from the group consisting of tetrahydrofurane, 2-methyl-tetrahydrofurane, tetrahydropyran, dimethyl ether, diethyl ether, methyl tert-butyl ether, ethyl acetate, γ-butyrolactone, methyl benzoate, dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, acetone, propiophenone, N-methylpyrrolidone, dimethyl acetamide, acetonitrile, butyronitrile, dimethyl sulfoxide, triethylamine and tetramethyl ethylene diamine, either in pure form or as a blend.

The invention is further directed to the use of an anhydrous rare-earth metal halide $REHal_3$ produced by the method of the invention, where RE and Hal are as defined in the invention, as a raw material for producing a specific rare-earth compound or as a catalyst in a polymerization reaction.

Preferred halogenating agents are the tetrahalogen compounds $MHal_4$ (M and Hal = meanings given above); $C_6H_5MHal_3$; $HMHal_3$; $C_6H_4HalMHal_3$ where C_6H_4Hal = e.g. chlorine, bromine or iodine phenyl; $(H_3C)_2MClCH_2Hal$; $(CH_3)_2MHal_2$; $(CH_3)_3MHal$ or mixtures thereof. Particularly preferred halogenating agents are:

$SiCl_4$, $SiBr_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $TiBr_4$, $C_6H_5SiCl_3$, 4-$ClC_6H_4SiCl_3$, 4-$BrC_6H_4SiCl_3$, $HSiCl_3$, $(H_3C)_2ClSiCH_2Cl$, $(H_3C)_2ClSiCH_2Br$, $(CH_3)_2SiCl_2$ or $(CH_3)_3SiCl$.

Ethereal compounds can be used as polar, aprotic solvents. These can be

- open-chain, such as R^1-O-R^2 (where R^1 and R^2 are mutually independently alkyl or aryl having 1 to 8 C atoms); or
- cyclic, such as 

(where n = 3 or 4 and R = H or alkyl having 1 to 8 C atoms); or
- polyfunctional, such as R-O-($-CH_2$-CH_2-O$)_n$-R' (where R and R' are mutually independently alkyl radicals having 1 to 8 C atoms and n = 1 to 100),

and used either in pure form or as a mixture. Tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran, dimethyl ether, diethyl ether or methyl tert-butyl ether or a mixture thereof, for example, can be used as the ethereal solvent.

The following aprotic, polar solvents can also be used:

- esters, e.g. carboxylic acid esters (such as ethyl acetate, γ-butyrolactone, methyl benzoate), or carbonic acid esters (such as dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate), or mixtures thereof; or
- ketones (e.g. acetone, propionone); or
- amides (e.g. N-methyl pyrrolidone, dimethyl acetamide, NMPU); or
- nitriles (e.g. acetonitrile, butyronitrile); or
- halogen-free sulfur compounds (e.g. dimethyl sulfoxide); or
- tertiary amines (e.g. triethylamine, tetramethyl ethylene diamine).

One or more hydrocarbons, such as e.g. alkanes (e.g. pentane, hexane, cyclohexane, methyl cyclohexane, heptane or octane) or aromatics (e.g. benzene, toluene, ethyl benzene, cumene or xylene) in the weight ratio of solvent to hydrocarbon of 1 : maximum 5, can optionally be added to the polar, aprotic solvents.

The compounds RE_2O_3, where RE = scandium, yttrium, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, generally in commercial form, are used as rare-earth metal oxides. They are preferably used in powdered form and anhydrously, in other words with H_2O contents of < 0.5 %. Nd_2O_3, Sm_2O_3 or La_2O_3 are particularly preferably used.

Surprisingly it was found that the above-mentioned rare-earth oxides in the form of a suspension in polar aprotic solvents react with the halogenating agents having formula (1) at temperatures as low as ≤ 30°C, for example, and yield the desired rare-earth metal halides in accordance with the reaction below:

$$n\,\mathrm{RE_2O_3} + \mathrm{n}\,\frac{6}{\mathrm{Y}}\,\mathrm{MHalX^1X^2X^3} \xrightarrow{\text{solvent}} 2\,n\,\mathrm{REHal_3} + \frac{6}{\mathrm{Y}}\,[\mathrm{M(O)_{1/2}X^4X^5X^6}]_\mathrm{n}$$

X^1, X^2, X^3 are mutually independently Cl, Br, I, H, alkoxy (-OR), wherein R represents an organic radical having 1-20 C atoms, alkyl having 1-20 C atoms or aryl having 6-20 C atoms, wherein the alkyl or aryl radicals can bear one or more further halogen substituents selected from the group comprising F, Cl, Br or I.

Y can assume the value 1, 2, 3 or 4 and is calculated from the number of halide atoms in the compound $MHalX^1X^2X^3$: Y = 1 + (number of substituents X^1, X^2, X^3 denoting halogen). If none of the substituents X^1, X^2 and X^3 is a halogen, then Y = 1; if all the substituents X^1, X^2 and X^3 are a halogen, then Y = 4.

In the reaction product $[M(O)_{1/2}X^4X^5X^6]_n$ the meaning of the radicals X^4, X^5 and X^6 is as follows:

For each substituent X^1, X^2 and/or X^3 of the halogenating agent that denotes a halogen (Cl, Br, I), the corresponding substituent X^4, X^5 and/or X^6 in the reaction product $[M(O)_{1/2}X^4X^5X^6]_n$ consists formally of half an oxygen atom $(O)_{1/2}$. This means that if X^1 = halogen, then $X^4 = (O)_{1/2}$, if X^2 = halogen, then $X^5 = (O)_{1/2}$ and if X^3 = halogen, then $X^6 = (O)_{1/2}$.

For each substituent X^1, X^2 and/or X^3 of the halogenating agent that does <u>not</u> denote a halogen (Cl, Br, I), the corresponding substituent X^4, X^5 and/or X^6 in the reaction product $[M(O)_{1/2}X^4X^5X^6]_n$ is unchanged. This means that if $X^1 \neq$ halogen, then $X^4 = X^1$; if $X^2 \neq$ halogen, then $X^5 = X^2$; and if $X^3 \neq$ halogen, then $X^6 = X^3$.

The above reaction equation gives the following theoretical stoichiometries for the various metal halide compounds $MHalX^1X^2X^3$:

X^1	X^2	X^3	theoretical molar ratio RE_2O_3 : $MHalX^1X^2X^3$
≠ Hal	≠ Hal	≠ Hal	1 : 6
= Hal	≠ Hal	≠ Hal	1 : 3
= Hal	= Hal	≠ Hal	1 : 2
= Hal	= Hal	= Hal	1 : 1.5

≠ Hal means "substituent not equal to halogen";
= Hal means "substituent equal to halogen"

It is sensible to maintain the theoretical reaction conditions to a large extent. In order to bring about a complete conversion to the rare-earth halide even in the case of poorly reactive raw material combinations, however, it is often sensible to use the metal halide compound in excess. In a preferred embodiment the metal halide compound is used in a 1 to 50% excess, based on the theoretical stoichiometries given in the table above.

Two examples of the general reaction equation described above are provided below:

a) X^1, X^2 and X^3 = Hal

$$2\,RE_2O_3 + 3\,MHal_4 \rightarrow 4\,REHal_3 + MO_2$$

b) $X^1 = C_6H_5$, X^2 and X^3 = Hal

$$n\,RE_2O_3 + 2\,n\,Hal_3MC_6H_5 \rightarrow 2\,n\,REHal_3 + 2\,[M(O)_{1.5}C_6H_5]_n$$

The simple mode of formation of the desired rare-earth metal halides is surprising because the *reverse* reaction in the absence of the solvent used in the method according to the invention is known from the literature. Thus Gmelin, Sc, Y, La-Lu, C4a, p. 152, describes how quartz and silicate glasses react with liquid and solid rare-earth metal chlorides at elevated temperatures according to the following equation:

$$2\,RECl_3\,(s,l) + SiO_2\,(s) \rightarrow 2\,MOCl\,(s) + SiCl_4\,(g)$$

A large number of oxide silicates and chlorosilicates (e.g. $Yb_3(SiO_4)_2Cl$) were also able to be formed.

By contrast, it was found here that rare-earth metal oxides with silicon tetrachloride, for example, in an aprotic, polar solvent (e.g. tetrahydrofuran (THF)) react quickly and irreversibly even at room temperature to form the desired rare-earth chlorides:

$$2\,RE_2O_3 + 3\,SiCl_4 \xrightarrow{THF} 4\,(RECl_3)_{THF} + 3\,SiO_2$$

The preferred reaction temperature is governed by the reactivity of the individual raw material combination. It is generally possible to work at room temperature. The reaction heat that is formed is dissipated by means of appropriate cooling. With specific raw material combinations, however, it may also be advisable to perform the reaction at low temperatures or in a heated environment. The internal temperature can be between -20 and 100°C, particularly preferably between 0 and 70°C.

It is also particularly surprising that the metal oxide that is formed as a by-product, e.g. SiO_2, initially occurs in soluble form, presumably as a metastably soluble polymer sol, in other words in a colloidal distribution. By contrast, the rare-earth metal halides have only a low solubility in the solvents or solvent blends used according to the invention, which means that the rare-earth metal halide in solid form, usually as a solvate with the aprotic polar solvent used, can be isolated in pure form by solid/liquid separation.

For example, in the reaction of Nd_2O_3 with $SiCl_4$ in THF, an $NdCl_3 \cdot 2$ THF complex is formed which is only slightly soluble in THF (approx. 1 to 1.5 wt.% based on $NdCl_3$) and which can be separated off in crystalline form by filtering the solvent and the SiO_2 sol and - depending on the precise reaction and processing conditions - isolated with yields of between approx. 60 and 90%.

It is often observed that the MO_2 by-product is dissolved as a sol for only a certain time (hours up to a few days) and then converts into gel form. Since a simple separation of the MO_2 by-product (e.g. by filtration, decantation or centrifuging) is no longer possible then, a particularly preferred embodiment of the present invention involves performing the solid/liquid separation *before* the conversion to the gel state.

Reaction mixtures in which the MO_2 by-product is already present in gel form can be processed by one of the methods described below, however:

a) separation of the MO_2 polymer by osmosis, i.e. membrane permeation, and/or

b) evaporation of the reaction mixture until dry and selective dissolution of the rare-earth metal halide.

For variant a), the MO_2-containing reaction mixture in sol or gel form should be purified by filtration through a semipermeable membrane, i.e. a membrane filter suitable for filtration and having a pore size of between 1 and 100 nm. Whilst the low-molecular-weight, soluble $MHal_3$ complex in dissolved form can pass through the pores, the MO_2 polymer is held back.

In variant b) the reaction mixture is partly or wholly evaporated in a temperature range of between 20 and 100°C, preferably under reduced pressure at the end. The remaining suspension or solid reaction mixture is then treated with a solvent which selectively dissolves the rare-earth metal halide. Suitable solvents here are, for example, ethers, alcohols, esters, ketones, amides, nitriles and amines and in principle also water. The latter is disadvantageous, however, because only rare-earth metal hydrates which can be converted back to the anhydrous compounds again by known means - albeit via a circuitous route - can be obtained in this way.

It was surprisingly also found that after total evaporation, the metal oxides formed as by-products no longer dissolve in pH-neutral solvents, i.e. ethers, alcohols, esters, ketones, nitriles, hydrocarbons, either in pure form or as a blend, so the rare-earth metal halides cannot be purified effectively by selective dissolution of the rare-earth halide in these solvents.

The process of extracting the soluble rare-earth metal component can take place in various ways by known methods:

- repeated suspension in the pH-neutral solvent and solid/liquid separation until no rare-earth metal compound can be detected in the filtrate
- extraction with boiling pH-neutral solvent, e.g. in a Soxhlet apparatus or extractor, or
- fixed-bed extraction, i.e. introducing the solid reaction mixture into a type of column and allowing a pH-neutral solvent to pass through it.

Organic solvents from the groups comprising ethers, alcohols, esters, ketones, nitriles and hydrocarbons, either in pure form or as a blend, are particularly suitable as pH-neutral solvents.

If the purity requirements are particularly high, the rare-earth metal halide/metal oxide mixture can also be purified by sublimation at ≥ 800°C under high vacuum. Whilst the rare-earth metal halide is volatile under these conditions, the oxide by-product is retained.

The rare-earth metal halides produced by the method according to the invention can be used as starting materials for the production of specific rare-earth metal compounds, such as rare-earth metal alkoxides, rare-earth metal amides and rare-earth metal alkyls and aryls, especially of cyclopentadiene compounds and compounds of benzoannelated cyclopentadiene derivatives such as indene or fluorene compounds. They can also be used directly as Lewis-acid catalysts in organic and inorganic synthesis chemistry.

Since the neutral metal oxide by-products have a non-disruptive effect on many reactions, the reaction or synthesis mixtures can also be used directly, i.e. without a prior purification stage, as reagents or catalysts. For cost reasons it is particularly preferably to produce the rare-earth halide compound *in situ* and to use it directly "in the same pot" for a subsequent chemical step, such as e.g. acetalisations, Friedel-Crafts reactions, etc.

The rare-earth metal halides produced according to the invention can be used for example as a reagent or catalyst for organic or inorganic reactions, as a raw material for the production of specific rare-earth compounds or as a catalyst in polymerisation reactions, for example in the production of polyolefins (polyethylene, polypropylene, EPDM and SBS copolymers) or in condensation polymerisation for the synthesis of polyesters such as polyethylene terephthalate, polyethylene naphthenate or polybutylene terephthalate.

The metal halide compounds are particularly preferably used for one of the following reactions: condensation reactions, aldol reactions, acetal formation, C-C coupling reactions and ring-opening reactions.

The subject-matter of the invention is described in more detail by means of the following examples:

Example 1: Production of $NdCl_3 \cdot 2$ THF from $Nd_2O_3/SiCl_4$ in THF

25.2 g (75 mmol) of neodymium oxide (99%, from Aldrich) were suspended in 140 g of THF in an inerted, i.e. dried and argon-filled, 0.5-litre double-jacket reactor with reflux condenser and dropping funnel. 20.5 g (120 mmol) of silicon tetrachloride were metered in with stirring within 30 minutes at internal temperatures of between 25 and 30°C.

The reaction was clearly exothermic and a light blue suspension was formed. On completion of the dropwise addition the mixture was stirred for a further 1.5 hours at approx. 30°C and then cooled to 20°C.

The suspension was then discharged onto a G3 sintered-glass filter and the crystalline filter residue rewashed once with 48 g of THF.

After vacuum drying for 4 hours at 25°C, 50.8 g of a finely crystalline, free-flowing powder were obtained.

Analysis: 2.65 mmol/g Nd; 7.51 mmol/g Cl; 52 ppm Si

(Theoretical for $NdCl_3 \cdot 2$ THF: 2.53 mmol/g Nd; 7.60 mmol/g Cl)

Yield: 90% of theoretical.

After being left to stand for two days, the initially somewhat liquid filtrates converted to gel form.

Example 2: Production of $NdCl_3 \cdot 2$ THF from Nd_2O_3 and $TiCl_4$/THF in THF suspension

968 g of a 0.28 molar titanium tetrachloride solution in THF (271 mmol) were placed in a 2-litre double-jacket reactor and 54.5 g (162 mmol) of neodymium oxide powder were added in portions (using a solids metering bulb) with stirring within approx. 40 minutes at internal temperatures of between 25 and 30°C.

After the release of heat had died down, stirring was continued for a further 30 minutes at approx. 25°C and the suspension was then filtered and the filter residue washed with 150 g of THF. 75.6 g of a powder were obtained after vacuum drying.

Analysis: Nd = 2.50 mmol/g, Cl = 7.50 mmol/g, Ti = 0.05 mmol/g

Yield: 58% of theoretical.

The product contained 0.4 wt.% of TiO_2.

After concentration in vacuo, cooling to 0°C and subsequent filtration, a further 32 g of a powder contaminated with 1.8 wt.% of TiO_2 were able to be obtained from the combined filtrates. The total yield was around 83% of theoretical.

Further examples according to the invention can be taken from the following two tables:

Table 1: Production of rare-earth halides

Exp. no.	RE oxide Type	RE oxide Amount (mmol)	Halogenating agent Type	Halogenating agent Amount (g)	Solvent Type	Solvent Amount (g)	Reaction conditions	Processing
3	Sm_2O_3	19.4	$SiCl_4$	29.4	THF	90	2 h refluxing	Filtration/ washing
4	Nd_2O_3	50	$PhSiCl_3$	100	THF	92	1 h 30°C, then 2 h refluxing	"
5	La_2O_3	102	$SiCl_4$	156	THF	334	Stirring approx. 25°C, then 1 h refluxing	Total evaporation/ Soxhlet extraction
6	La_2O_3	100	$SiCl_4$	158	THF	248	Stirring approx. 25°C, then 3 h refluxing	Filtration/ washing
7	La_2O_3	50	$SiCl_4$	78.9	THF/ toluene	160	As exp. 6	"
8	La_2O_3	50	$SiCl_4$	79	Acetone	296	3 h 20-50°C	"
9	La_2O_3	50	$SiCl_4$	78.5	DMC	171	1 h approx. 25°C, then 1.5 h refluxing	"
10	La_2O_3	30	$SiBr_4$	45	2-MeTHF	132	3 h 25°C, then 1 h refluxing	"
11	La_2O_3	50	$Me_2Si(CH_2Cl)Cl$	300	THF	120	8 h refluxing	"

Table 2: Reaction results for the rare-earth halide syntheses

Exp. no.	Product Appearance	Product Amount (g)	Analysis (mmol/g) RE	Analysis (mmol/g) Hal	Analysis (mmol/g) Si	Composition $REHal_3$ - *n* donor	Yield (% of theor.)
3	light yellow powder	12.5	2.6 (Sm)	7.3 (Cl)	0.10	$SmCl_3 \cdot 2$ THF	84
4	light blue powder	36.5	2.45 (Nd)	7.5 (Cl)	0.05	$NdCl_3 \cdot 2$ THF	89
5	white powder	28	2.80 (La)	8.60 (Cl)	0.15	$LaCl_3 \cdot 2$ THF	38
6	white powder	47.9	2.60 (La)	7.4 (Cl)	≤ 0.05	$LaCl_3 \cdot 2$ THF	62
7	"	31.7	2.58 (La)	7.70 (Cl)	0.01	$LaCl_3 \cdot 2$ THF	82
8	bulky, white	37.0	2.40 (La)	7.20 (Cl)	1.80	$LaCl_3 \cdot 2.5$ acetone*	89
9	white powder	27.6	2.45 (La)	6.90 (Cl)	0.08	$LaCl_3 \cdot 1.6$ DMC	67
10	white powder	9.3	1.97 (La)	5.70 (Br)	0.02	$LaBr_3 \cdot 2$ THF	31
11	white powder	31	2.71 (La)	8.10 (Cl)	0.10	$LaCl_3 \cdot 2$ THF	84

* contains approx. 8% SiO_2

In experiment 3 samarium oxide was used instead of Nd_2O_3 and $SmCl_3$ in the form of the THF complex was obtained as the reaction product.

In experiment 4 an organo-substituted silyl halide ($C_6H_5SiCl_3$) was used instead of $SiCl_4$ which after brief refluxing converted neodymium oxide into the chloride.

For examples 5 to 11 powdered lanthanum oxide was used. Experiments 6, 7, 8 and 9 differ from one another in the choice of reaction solvent: THF, THF-toluene, acetone and DMC are similarly suitable. If acetone is used, the by-product SiO_2 is precipitated out at the same time as the $LaCl_3$ crystallisate.

In experiment 5 a special processing method was chosen; after reacting the reactants La_2O_3 and $SiCl_4$ in THF, the reaction suspension formed was totally evaporated in a rotary evaporator at a bath temperature of 60°C and under a final pressure of 14 mbar. The solid, white residue was ground in an argon-filled glove box and then extracted with boiling THF in a Soxhlet apparatus for approx. 30 hours. A suspension was formed in this way which was filtered after cooling. The solid filter residue was washed with THF and dried at room temperature to constant weight. 28.0 g of a fine white powder were obtained with the composition given in Table 2.

Example 10 shows the production of a rare-earth bromide, in this case $LaBr_3$, which was produced using the brominating agent $SiBr_4$.

Finally, example 11 shows the use of an organosilicon chloride in which the organic radical is itself functionalised (with chloride).

WHAT IS CLAIMED IS:

1. A method for producing anhydrous rare-earth metal halides ($REHal_3$), comprising reacting a rare-earth metal oxide of the formula RE_2O_3, wherein RE is Sc, Y, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, with a halogenating agent of the formula (1):

$$MHalX^1X^2X^3 \quad (1)$$

wherein:

M is Si, Ge, Sn, Ti, Zr or Hf;

Hal is Cl, Br or I; and

X1, X2 and X3 are each independently Cl, Br, I, H, alkoxide –OR wherein R is an organic radical having 1-20 C atoms, an alkyl having 1-20 C atoms, or an aryl having 6-20 C atoms; wherein the alkyl or aryl radicals are optionally substituted at least once with F, Cl, Br or I;

in one or more of an aprotic, polar solvent.

2. The method according to claim 1, wherein the halogenating agent is a tetrahalogen compound of the formula $MHal_4$.

3. The method according to claim 1, wherein the halogenating agent is selected from the group consisting of C_6H_5 $MHal_3$, $HMHal_3$, $C_6H_4HalMHal_3$, $(H_3C)_2MaCH_2Hal$, $(CH_3)_2$ $MHal_2$ and $(CH_3)_3MHal$.

4. The method according to claim 1, wherein the halogenating agent is selected from the group consisting of $SiCl_4$, $SiBr_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $TiBr_4$, $C_6H_5SiCl_3$, 4-$ClC_6H_4SiCl_3$, 4-$BrC_6H_4SiCl_3$, $HSiCl_3$, $(H_3C)_2ClSiCH_2C$, $(H_3C)_2ClSiCH_2Br$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$.

5. The method according to any one of claims 1 to 4, wherein said one or more of the aprotic, polar solvent comprises at least one of an ester, a carbonic acid

ester, a ketone, an amide, a nitrile, a halogen-free sulfur compound or a tertiary amine.

6. The method according to any one of claims 1 to 5, wherein the one or more aprotic, polar solvent comprises at least one of tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran, dimethyl ether, diethyl ether and methyl tert-butyl ether.

7. The method according to any one of claims 1 to 6, wherein one or more hydrocarbons are added to the one or more polar, aprotic solvent in the weight ratio of 1 part of polar, aprotic solvent to a maximum of 5 parts of hydrocarbon.

8. The method according to claim 7, wherein the one or more hydrocarbons are at least one of an alkane or an aromatic.

9. The method according to any one of claims 1 to 8, wherein the rare-earth metal oxide is in powdered form and has a residual water content of <0.5 wt. %.

10. The method according to any one of claims 1 to 9, wherein the rare earth oxide is Nd_2O_3, Sm_2O_3 or La_2O_3.

11. The method according to any one of claims 1 to 10, wherein the molar ratio between the rare-earth oxide RE_2O_3 and the halogenating agent $MHalX^1X^2X^3$ is chosen as follows:

approximately 1:6 for X^1, X^2, $X^3 \neq$ Hal;
approximately 1:3 for X^1=Hal, X^2, $X^3 \neq$ Hal;
approximately 1:2 for X^1, X^2=Hal, $X^3 \neq$ Hal; or
approximately 1:1.5 for X^1, X^2, X^3=Hal.

12. The method according to any one of claims 1 to 10, wherein the halogenating agent is used in an excess of 1 to 50 mol %.

13. The method according to any one of claims 1 to 12, wherein the reaction is performed at a temperature in a range from -20 to +100°C.

14. The method according to claim 13, wherein the reaction temperature is in the range from 0 to 70°C.

15. The method according to any one of claims 1 to 14, wherein after the end of the conversion but before the start of any gelling process that might begin, the rare-earth metal halide is separated from the solution of the metal oxide by-product by means of a solid/liquid separation.

16. The method according to claim 15, wherein the solid rare-earth metal halide is purified by washing with an aprotic solvent.

17. The method according to claim 16, wherein the purification is on a filter, in a Soxhlet extractor or in a column by fixed-bed extraction.

18. The method according to any one of claims 1 to 17, wherein after an exothermic reaction has died down, the reaction mixture is evaporated until dry.

19. The method according to claim 18, wherein the evaporation is performed in the temperature range between 20 and 100°C and at least partly under reduced pressure.

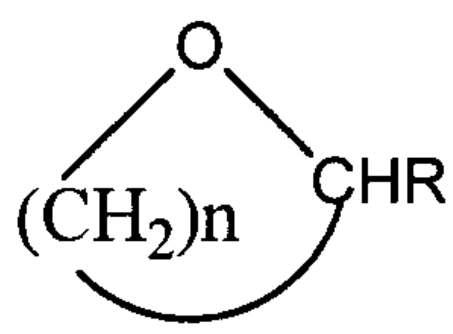
20. The method according to claim 18, wherein the rare-earth halide is obtained from the evaporation residue by extraction with a pH-neutral solvent.

21. The method according to claim 20, wherein the pH-neutral solvent contains one or more substances selected from the group consisting of ethers, alcohols, esters, ketones and nitriles and optionally additionally one or more hydrocarbons.

22. The method according to any one of claims 1 to 21, wherein the rare-earth metal halide/metal oxide mixture is further purified by sublimation at ≥ 800°C under high vacuum.

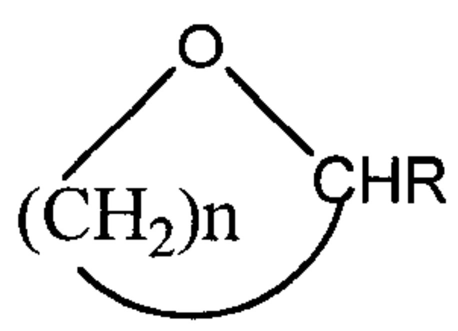
23. The method according to claim 1, wherein the polar, aprotic solvent comprises at least one of the formula:

R^1—O—R^2 wherein R^1 and R^2 are mutually independently alkyl or aryl having 1 to 8 C atoms;

cyclic , where n=3 or 4 and R=H or alkyl having from 1 to 8 C atoms; or

polyfunctional, R—O—(—CH_2—CH_2—O$)_n$—R', where R and R' are mutually independently alkyl radicals having 1 to 8 C atoms and n is from 1 to 100;

and used either in pure form or as a mixture.

24. The method according to claim 23, wherein the polar, aprotic solvent comprises said  , where R and n are as defined in claim 23.

25. The method according to claim 23, wherein said pure form is used.

26. The method according to claim 23, wherein said mixture is used.

27. Use of a reaction mixture comprising a rare-earth oxide of formula RE_2O_3, a halogenating agent and a polar, aprotic solvent or an aprotic solvent blend, as a reagent or catalyst in an organic or inorganic reaction, wherein

RE is selected from the group consisting Sc, Y, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

the halogenating agent is selected from the group consisting of $SiCl_4$, $SiBr_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $TiBr_4$, $C_6H_5SiCl_3$, 4-$ClC_6H_4SiCl_3$, 4-$BrC_6H_4SiCl_3$, $HSiCl_3$, $(H_3C)_2ClSiCH_2Cl$, $(H_3C)_2ClSiCH_2Br$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$; and

the polar, aprotic solvent or the aprotic solvent blend is selected from the group consisting of tetrahydrofurane, 2-methyl-tetrahydrofurane, tetrahydropyran, dimethyl ether, diethyl ether, methyl tert-butyl ether, ethyl acetate, γ-butyrolactone, methyl benzoate, dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, acetone, propiophenone, N-methylpyrrolidone, dimethyl acetamide, acetonitrile, butyronitrile, dimethyl sulfoxide, triethylamine and tetramethyl ethylene diamine, either in pure form or as a blend.

28. The use according to claim 27, wherein the organic or inorganic reaction is a condensation, aldol reaction, acetal formation, C—C coupling or ring-opening reaction.