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(54) **Title:** PROCESS FOR THE PRODUCTION OF DIALKYL ZINC AND DIALKYL ALUMINIUM HALIDE

(57) **Abstract:** Process for the production of dialkyl zinc and dialkyl aluminium halide by reacting zinc halide with trialkyl aluminium to form dialkyl zinc and dialkyl aluminium halide, followed by removal of dialkyl zinc from the reaction mixture by distillation, wherein the trialkyl aluminium has been pre-treated with an alkyne.



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PROCESS FOR THE PRODUCTION OF DIALKYL ZINC AND DIALKYL ALUMINIUM HALIDE

The present invention relates to a process for the production of dialkyl zinc and
5 dialkylaluminium halide, a method of reducing the hydride content of trialkyl
aluminium, and a trialkyl aluminium-containing formulation.

In recent years, the demand for dialkyl zinc has grown because of its use as a
catalyst or reagent for polymerization and pharmaceuticals manufacturing and its
10 use in the production of solar cells and semiconductor devices.

Dialkyl zinc is generally prepared by reacting zinc dihalide (e.g. ZnCl_2) with trialkyl
aluminium to form both dialkyl zinc and dialkyl aluminium halide. Dialkyl zinc can
be removed from the resulting reaction mixture by distillation. This process has
been disclosed in various documents, e.g. US 3,124,604 and EP 2 223 024.

15 The other product, dialkyl aluminium halide, is also valuable and finds application
as a co-catalyst in alkene polymerization. For these applications, dialkyl aluminium
halide is desired to be as pure as possible.

Trialkyl aluminium is the product obtained from the reaction of aluminium with
20 hydrogen and alkene, and as a result it generally contains hydrides such as R_2AlH ,
 RAlH_2 , and AlH_3 as impurities; the main impurity being R_2AlH . The use of a trialkyl
aluminium with a high hydride concentration for the reaction with zinc chloride
leads to precipitation of metallic zinc, resulting in reactor fouling and a lower dialkyl
zinc yield.

25

It is therefore desired to reduce the hydride concentration of trialkyl aluminium.

A method to achieve this has been disclosed in WO 2009/133929 and involves the
reaction between trialkyl aluminium with a hydride content of 0.40-1.0 wt% and

ethylene with a partial pressure of 0.1-0.6 MPa, at a temperature of 65-95°C, and for a time period of 1-10 hours.

It is an object of the present invention to provide a method for reducing the hydride
5 concentration of trialkyl aluminium which is more convenient, can be performed at room temperature and atmospheric pressure, and/or results in even lower hydride concentrations.

It has now been found that this object can be met by reacting the trialkyl aluminium
10 with an alkyne.

With this method, the hydride concentration of trialkyl aluminium can be reduced to less than 0.010 wt%, preferably less than 0.008 wt%, more preferably less than 0.005 wt%, and most preferably even less than 0.003 wt%.

The hydride concentration is expressed as wt% AlH_3 . The hydride concentration is
15 determined by introducing water into a sample - the water will hydrolyze any trialkyl aluminium and any aluminium hydrides – and analyzing any evolved gases (hydrogen, alkane) by gas chromatography. From the gas composition, one can calculate the amount of hydrides that must have been present in the sample.

20 The alkyl groups of trialkyl aluminium is not limited in nature, but alkyl groups with 1 to 5 carbon atoms are generally preferred, 2-5 carbon carbon atoms are even more preferred. The most preferred trialkyl aluminium is triethyl aluminium. Conventional commercial triethyl aluminium contains about 0.01 to 0.05 wt% hydride.

25

The term “alkyne” includes monoalkynes, dialkynes, etc. The alkyne preferably has 2 to 200, more preferably 3-200, even more preferably 4-100, even more preferably 4-50, and most preferably 4-18 carbon atoms.

Examples of suitable alkynes are acetylene, 1-propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 1-hexyne, 2-hexyne, 3-hexyne, 1-heptyne, 2-heptyne, 3-heptyne, 1-octyne, 2-octyne, 3-octyne, 4-octyne, 1-decyne, 5-decyne, 1-tetradecyne, 1,6-heptadiyne, 1,7-octadiyne, 1-octadecyne, phenylacetylene, 5 diphenylacetylene, 4-ethynylbiphenyl. Terminal alkynes are preferred over non-terminal alkynes.

Also mixtures of alkynes may be used.

Alkynes reduce the hydride content significantly faster than alkenes. As a 10 consequence, they are able to reduce the hydride content at lower temperatures and in a shorter time period.

The alkyne preferably has a boiling point of either significantly below the boiling point of the dialkyl zinc, or significantly above the boiling point of the dialkyl 15 aluminium halide that will result from the process of the present invention. If the products resulting from the process are diethyl zinc and diethyl aluminium chloride, the boiling point of the alkyne preferably lies below 100°C (boiling point of diethyl zinc is 118°C) or above 230°C (boiling point of diethylaluminium chloride is 214°C), more preferably below 90°C or above 240°C. In this way, the alkyne can be easily 20 removed by either distillation (if the boiling point is below that of the dialkyl zinc) or by remaining in the bottoms (if the boiling point is above that of dialkyl aluminium halide).

The term "boiling point" in this specification refers to the boiling point at atmospheric pressure.

25

The trialkyl aluminium is pre-treated with the alkyne under inert atmosphere in a weight ratio trialkyl aluminium : alkyne of at least 50:50, preferably at least 80:20, even more preferably at least 90:10, and most preferably at least 99.7:0.3.

A solvent can be present during this pre-treatment. Suitable solvents include aromatic and saturated aliphatic hydrocarbons. Specific examples of suitable solvents are n-hexane, cyclohexane, n-heptane, n-octane, n-decane, n-dodecane, n-tetradecane, 2-methylhexane, 3-methylhexane, 2,2-dimethylpentane, 2,2,3-trimethylbutane, 3-ethylpentane, decahydronaphthalene, benzene, toluene, xylene, methylnaphthalene, and THF.

Pre-treatment of trialkyl aluminum with an alkyne is preferably performed at a temperature in the range 0-130°C, more preferably 10-100°C, and most preferably 20-50°C and for a preferred period of 0.1-1000 hours, more preferably 1-100 hours, and most preferably 5-40 hours.

The present invention therefore also relates to a method of reducing the hydride content of trialkyl aluminium by contacting the trialkyl aluminium with an alkyne for a period of 0.1-1000 hrs at a temperature in the range 0-130°C.

The present invention also relates to a storage stable formulation comprising trialkyl aluminium and an alkyne, more preferably a formulation comprising 5-99.7 wt% of trialkyl aluminium, 0.3-50 wt% of an alkyne with 3-200 carbon atoms, and 0-94.7 wt% of a solvent.

“Storage stable formulation” is defined in this specification as a formulation which can be stored at 20°C under nitrogen atmosphere (<2 ppm oxygen) for 5 days without any significant change in its chemical or physical constitution, except for the reduction in hydride content.

Dialkyl zinc is generally prepared by reacting zinc dihalide (preferably ZnCl_2) with trialkyl aluminium to form both dialkyl zinc and dialkyl aluminium halide. This reaction is preferably performed in a dry, i.e. non-aqueous, inert gas atmosphere. An organic solvent may be present during the reaction.

The reaction is preferably performed at a temperature in the range 20 to 100°C, more preferably 30 to 70°C. The amount of trialkyl aluminum is preferably 1.6 to 2.4 moles, more preferably 1.8 to 2.2 moles per 1 mole of the zinc halide. The reaction is complete when the zinc halide has dissolved in the reaction mixture.

5 This may take about 5 minutes to 15 hours, depending on the reaction conditions.

After completion of the reaction, the formed dialkylzinc is distilled from the reaction mixture. Before said distillation, it is preferred to separate and remove any precipitates contained in the reaction product by, e.g., filtration. To prevent thermal decomposition of the dialkyl zinc or dialkyl aluminum halide, it is preferred to

10 perform the distillation under reduced pressure.

After having distilled the dialkyl zinc from the reaction mixture, the residue might be distilled again, also at reduced pressure, in order to remove and purify the dialkyl aluminium halide.

15 Dialkyl zinc has the formula R_2Zn , in which R denotes an alkyl group. This alkyl group preferably has 1-5 carbon atoms, and most preferably is ethyl.

EXAMPLES

20 Comparative Example 1

A vial was filled with 0.46 g 1-octene and 43.78 g triethyl aluminium with a hydride content of 0.022 wt% under nitrogen atmosphere in a glove box. The vial was kept for 10 days at room temperature, followed by 64 hours at 60°C, and samples were taken at regular time intervals. These samples were analyzed for their hydride
25 content by gas chromatography according to the method described in the specification.

The results are displayed in Table 1.

Table 1

	Wt% hydride
t=0	0.0220
After 1 day at RT	0.0201
After 2 days at RT	0.0196
After 3 days at RT	0.0189
After 6 days at RT	0.0187
After 10 days at RT	0.0185
64 hrs at 60°C	0.0080

Example 2

Vials were filled with different amounts of 1-decyne and triethyl aluminium (TEAL) with a hydride content of 0.0178 wt% hydride under nitrogen atmosphere in a glove box. These vials were kept for 9 days at room temperature, and samples were taken at regular time intervals. These samples were analyzed for their hydride content as described in Example 1.

The results are displayed in Table 2.

Table 2

1-decyne/TEAL weight ratio	1-decyne : DEAL-H molar ratio	Wt% hydride				
		0 days	2 days	5 days	7 days	9 days
0.0010	0.5:1	0.0178	0.0131	0.0140	0.0132	0.0126
0.0025	1:1	0.0178	0.0120	0.0107	0.0089	0.0093
0.0050	2:1	0.0178	0.0116	0.0078	0.0072	0.0058
0.0075	3:1	0.0178	0.0083	0.0068	0.0052	0.0060
0.0105	4:1	0.0178	0.0065	0.0044	0.0036	0.0025

Example 3

Vials were filled - under nitrogen atmosphere in a glove box - with 20 g triethyl aluminium (TEAL) with a hydride content of 0.0335 wt% and an amount of aliphatic unsaturated hydrocarbon corresponding to a diethylaluminium hydride/unsaturation mole ratio of 2:1. These vials were kept for 9 days at room temperature, and samples were taken at regular time intervals. These samples were analyzed for their hydride content as described in Example 1.

10

The results are displayed in Table 3.

Table 3

		Wt% Hydride			
	wt. (g)	3 days	6 days	9 days	13 days
1-Decyne	0.20	0.0138	0.0097	0.0065	0.0067
5-Decyne	0.19	0.0268	0.0244	0.0208	0.0191
1-Octene	0.15	0.0317	0.0299	0.0275	0.0269
cis-Cyclooctene	0.15	0.0326	0.0333	0.0321	0.0339
1,7-Octadiene	0.07	0.0317	0.0298	0.0284	0.0293
1-Heptyne	0.13	0.0123	0.0102	0.0064	0.0068
1-Octyne	0.15	0.0132	0.0100	0.0068	0.0058
1,7-Octadiyne	0.07	0.0169	0.0123	0.0090	0.0107

The results in the Table show that alkynes have a higher activity than alkenes and that terminal alkynes perform the best.

CLAIMS

1. Process for the production of dialkyl zinc and dialkyl aluminium halide by reacting zinc halide with trialkyl aluminium to form dialkyl zinc and dialkyl aluminium halide, followed by removal of dialkyl zinc from the reaction mixture by distillation, wherein said trialkyl aluminium has been pre-treated with an alkyne.
5
2. Process according to claim 1 wherein the alkyne is selected from the group consisting of 1-hexyne, 2-hexyne, 1-heptyne, 2-heptyne, 1-octyne, 1-decyne, 5-decyne, and 1,7-octadiyne.
10
3. Process according to any one of the preceding claims wherein the pre-treatment of the trialkyl aluminium with the alkyne is conducted by contacting the trialkyl aluminium with the alkyne for a period of 0.1-1000 hrs at a temperature in the range 0-150 °C.
15
4. Process according to claim 3 wherein the trialkyl aluminium and the alkyne are contacted for a period of 0.1-1000 hrs at a temperature in the range 0-130 °C.
20
5. Method of reducing the hydride content of trialkyl aluminium by contacting the trialkyl aluminium with an alkyne for a period of 0.1-1000 hrs at a temperature in the range 0-130 °C.
25
6. Method according to claim 5 wherein the alkyne is selected from the group consisting of 1-hexyne, 2-hexyne, 1-heptyne, 2-heptyne, 1-octyne, 1-decyne, 5-decyne, and 1,7-octadiyne.

7. Storage stable formulation comprising trialkyl aluminium and an alkyne.
8. Formulation according to claim 7 comprising 5-99.7 wt% of trialkyl
5 aluminium, 0.3-50 wt% of alkyne, and 0-94.7 wt% of solvent.
9. Formulation according to claim 7 or 8 wherein the alkyl groups of the trialkyl aluminium have 2-5 carbon atoms.
- 10 10. Formulation according to claim 9 wherein the trialkyl aluminium is triethyl aluminium.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/056115

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F3/06 C07F5/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, EMBASE, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

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International application No

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