

Process for the Generation of Metal- or Semimetal-containing Films

Description

- 5 The present invention is in the field of processes for the generation of inorganic metal- or semi-metal-containing films on substrates, in particular atomic layer deposition processes.

With the ongoing miniaturization, e.g. in the semiconductor industry, the need for thin inorganic films on substrates increases while the requirements on the quality of such films become
10 stricter. Thin metal or semimetal films serve different purposes such as barrier layers, conducting features, or capping layers. Several methods for the generation of metal or semimetal films are known. One of them is the deposition of film forming compounds from the gaseous state on a substrate. In order to bring metal or semimetal atoms into the gaseous state at moderate temperatures, it is necessary to provide volatile precursors, e.g. by complexation of the metals or
15 semimetals with suitable ligands. These precursors need to be sufficiently stable for evaporation, but on the other hand they need to be reactive enough to react with the surface of deposition.

EP 3 121 309 A1 discloses a process for depositing aluminum nitride films from tris(dialkylamino)aluminum precursors. However, the precursor is not stable enough for applications which
20 require high quality films.

In order to convert deposited metal or semimetal complexes to metal or semimetal films, it is usually necessary to expose the deposited metal or semimetal complex to a reducing agent.
25 Typically, hydrogen gas is used to convert deposited metal or semimetal complexes to metal or semimetal films. While hydrogen works reasonably well as reducing agent for relatively noble metals like copper or silver, it does not yield satisfactory results for more electropositive metals such as titanium or aluminum.

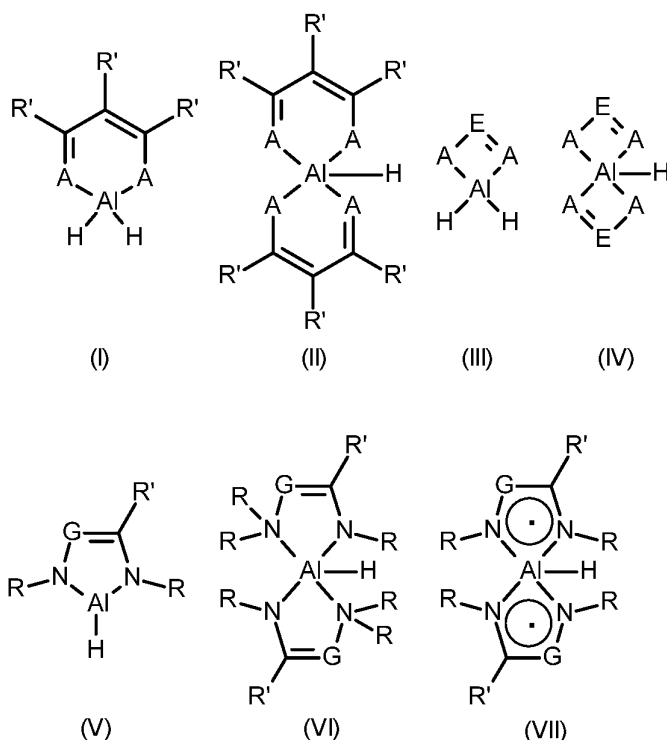
30 WO 2013 / 070 702 A1 discloses a process for depositing metal films employing aluminum hydride which is coordinated by a diamine as reducing agent. While this reducing agent generally yields good results, for some demanding applications, higher vapor pressures, stability and/or reduction potential is required.

35 N. Kuhn et al. disclose in Zeitschrift für Anorganische und Allgemeine Chemie, volume 626 (2000) page 1387-1392 vinamidin-alane complexes. However, their suitability for preparing inorganic metal- or semimetal-containing films is not recognized by the authors.

40 It was therefore an object of the present invention to provide a process for preparing inorganic metal- or semimetal-containing films having less impurity in the film. The process materials should be easy to handle; in particular, it should be possible to vaporize them with as little decomposition as possible. Further, the process material should not decompose at the deposition surface under process conditions but at the same time it should have enough reactivity to participate in the surface reaction. All reaction by-products should be volatile to avoid film contamination.
45 In addition, it should be possible to adjust the process such that metal or semimetal atoms

in the process material are either volatile or are incorporated in the film. Furthermore, the process should be versatile, so it can be applied to produce a broad range of different metals including electropositive metal or semimetal films.

- 5 These objects were achieved by a process for preparing inorganic metal- or semimetal-containing films comprising
- (a) depositing a metal- or semimetal-containing compound from the gaseous state onto a solid substrate and
- (b) bringing the solid substrate in contact with a compound of general formula (I), (II), (III), (IV),
- 10 (V), (VI), or (VII) in the gaseous state



15 wherein A is NR or O,

E is CR'', CNR''₂, N, PR''₂, or SOR'',

G is CR' or N,

R is an alkyl group, an alkenyl group, an aryl group, or a silyl group and

- 20 R' and R'' are hydrogen, an alkyl group, an alkenyl group, an aryl group, or a silyl group.

The invention further relates to the use of a compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) as reducing agent in a vapor deposition process.

- 25 Preferred embodiments of the present invention can be found in the description and the claims. Combinations of different embodiments fall within the scope of the present invention.

The process according to the present invention is suitable for preparing inorganic metal- or semimetal-containing films. Inorganic in the context of the present invention refers to materials which contain at least 5 wt.-% of at least one metal or semimetal, preferably at least 10 wt.-%, more preferably at least 20 wt.-%, in particular at least 30 wt.-%. Inorganic films typically contain carbon only in the form of a carbide phase including mixed carbide phases such as nitride carbide phases. The carbon content of carbon which is not part of a carbide phase in an inorganic film is preferably less than 5 wt.-%, more preferable less than 1 wt.-%, in particular less than 0.2 wt.-%. Preferred examples of inorganic metal- or semimetal-containing films are metal or semimetal nitride films, metal or semimetal carbide films, metal or semimetal carbonitride films, metal or semimetal alloy films, intermetallic compound films or films containing mixtures thereof.

The film prepared by the process according to the present invention contains metal or semimetal. It is possible that the film contains one metal or semimetal or more than one metal and/or semimetal. Metals include Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Bi. Semimetals include B, Si, Ge, As, Sb, Se, Te. Preferably, the metal- or semimetal is more electropositive than Cu, more preferably more electropositive than Ni. In particular, the metal or semimetal is Ti, Ta, Mn, Mo, W, Ge, Ga, As, In, Sb, Te, Al or Si.

The solid substrate can be any solid material. These include for example metals, semimetals, oxides, nitrides, and polymers. It is also possible that the substrate is a mixture of different materials. Examples for metals are aluminum, steel, zinc, and copper. Examples for semimetals are silicon, germanium, and gallium arsenide. Examples for oxides are silicon dioxide, titanium dioxide, and zinc oxide. Examples for nitrides are silicon nitride, aluminum nitride, titanium nitride, and gallium nitride. Examples for polymers are polyethylene terephthalate (PET), polyethylene naphthalene-dicarboxylic acid (PEN), and polyamides.

The solid substrate can have any shape. These include sheet plates, films, fibers, particles of various sizes, and substrates with trenches or other indentations. The solid substrate can be of any size. If the solid substrate has a particle shape, the size of particles can range from below 100 nm to several centimeters, preferably from 1 μ m to 1 mm. In order to avoid particles or fibers to stick to each other while the metal- or semimetal-containing compound is deposited onto them, it is preferably to keep them in motion. This can, for example, be achieved by stirring, by rotating drums, or by fluidized bed techniques.

According to the present invention the solid substrate is brought in contact with a compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) in the gaseous phase. R' in the compound of general formula (I) or (II) is hydrogen, an alkyl group, an alkenyl group, an aryl group, or a silyl group, preferably hydrogen or an alkyl group, in particular hydrogen, methyl or ethyl. The R' can be the same or different to each other. Preferably, all R' are the same.

An alkyl group can be linear or branched. Examples for a linear alkyl group are methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl. Examples for a branched

alkyl group are iso-propyl, iso-butyl, sec-butyl, tert-butyl, 2-methyl-pentyl, neo-pentyl, 2-ethyl-hexyl, cyclopropyl, cyclohexyl, indanyl, norbornyl. Preferably, the alkyl group is a C₁ to C₈ alkyl group, more preferably a C₁ to C₆ alkyl group, in particular a C₁ to C₄ alkyl group, such as methyl, ethyl, iso-propyl or tert-butyl.

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An alkenyl group contains at least one carbon-carbon double bond. The double bond can include the carbon atom with which R' is bound to the rest of the molecule, or it can be placed further away from the place where R' is bound to the rest of the molecule. Alkenyl groups can be linear or branched. Examples for linear alkenyl groups in which the double bond includes the carbon atom with which R' is bound to the rest of the molecule include 1-ethenyl, 1-propenyl, 1-n-butenyl, 1-n-pentenyl, 1-n-hexenyl, 1-n-heptenyl, 1-n-octenyl. Examples for linear alkenyl groups in which the double bond is placed further away from the place where R' is bound to the rest of the molecule include 1-n-propen-3-yl, 2-buten-1-yl, 1-buten-3-yl, 1-buten-4-yl, 1-hexen-6-yl. Examples for branched alkenyl groups in which the double bond includes the carbon atom with which R' is bound to the rest of the molecule include 1-propen-2-yl, 1-n-buten-2-yl, 2-buten-2-yl, cyclopenten-1-yl, cyclohexen-1-yl. Examples for branched alkenyl groups in which the double bond is placed further away from the place where R' is bound to the rest of the molecule include 2-methyl-1-buten-4-yl, cyclopenten-3-yl, cyclohexene-3-yl. Examples for an alkenyl group with more than one double bond include 1,3-butadien-1-yl, 1,3-butadien-2-yl, cyclopentadien-5-yl.

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Aryl groups include aromatic hydrocarbons such as phenyl, naphthalyl, anthracenyl, phenanthrenyl groups and heteroaromatic groups such as pyrrolyl, furanyl, thienyl, pyridinyl, quinoyl, benzofuryl, benzothiophenyl, thienothieryl. Several of these groups or combinations of these groups are also possible like biphenyl, thienophenyl or furanylthienyl. Aryl groups can be substituted for example by halogens like fluoride, chloride, bromide, iodide; by pseudohalogens like cyanide, cyanate, thiocyanate; by alcohols; alkyl chains or alkoxy chains. Aromatic hydrocarbons are preferred, phenyl is more preferred.

25

A silyl group is a silicon atom with typically three substituents. Preferably a silyl group has the formula SiX₃, wherein X is independent of each other hydrogen, an alkyl group, an aryl group or a silyl group. It is possible that all three X are the same or that two X are the same and the remaining X is different or that all three X are different to each other, preferably all X are the same. Alkyl and aryl groups are as described above. Examples for silyl groups include SiH₃, methylsilyl, trimethylsilyl, triethylsilyl, tri-n-propylsilyl, tri-iso-propylsilyl, tricyclohexylsilyl, dimethyl-tert-butylsilyl, dimethylcyclohexylsilyl, methyl-di-iso-propylsilyl, triphenylsilyl, phenylsilyl, dimethylphenylsilyl, pentamethyldisilyl.

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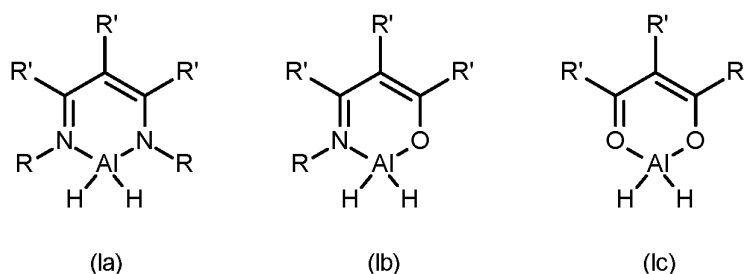
A in the compound of general formula (I), (II), (III) or (IV) is NR or O, i.e. a nitrogen atom bearing a substituent R or an oxygen atom. R is an alkyl group, an alkenyl group, an aryl group, or a silyl group. The same definitions apply as for R' described above. Preferably, R is an alkyl or silyl group, more preferably methyl, ethyl, iso-propyl, sec-butyl, tert-butyl or trimethylsilyl, in particular tert-butyl or trimethylsilyl.

40

E in the compound of general formula (III) or (IV) is CR'', CNR''₂, N, PR''₂, or SOR'' i.e. a carbon atom bearing one substituent R'' or a carbon atom bond to a nitrogen atom bearing two substituents R'', a nitrogen atom, a phosphor atom bearing two substituents R'', or a sulfur atom bearing an oxygen atom via a double bond and a substituent R''. The same definitions apply as for R' described above. Preferably, R'' is an alkyl or aryl group, in particular methyl or ethyl.

It is possible that all R, R' and R'' are separate substituents. Alternatively, it is possible that two of R, R' and R'' together form a ring, preferably a four to eight-membered ring, in particular a five- or six-membered ring.

Preferably, the central R', i.e. the R' in the 3 position of the ligand, in the compound of general formula (I) is H. The compound of general formula (I) comprises the following general formulae.



Preferred examples for the compound of general formula (I) with reference to these general formulae are given in the following table.

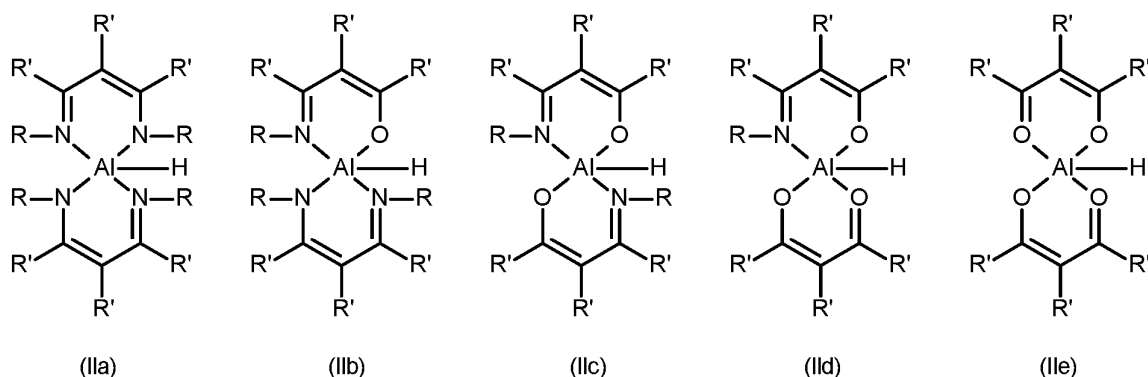
No.	Formula	R	R'
Ia-1	Ia	iPr	CH ₃ , H, CH ₃
Ia-2	Ia	sBu	CH ₃ , H, CH ₃
Ia-3	Ia	tBu	CH ₃ , H, CH ₃
Ia-4	Ia	TMS	CH ₃ , H, CH ₃
Ia-5	Ia	iPr	CF ₃
Ia-6	Ia	tBu	CF ₃
Ia-7	Ia	iPr	DIP
Ib-1	Ib	iPr	CH ₃ , H, CH ₃
Ib-2	Ib	sBu	CH ₃ , H, CH ₃
Ib-3	Ib	tBu	CH ₃ , H, CH ₃
Ib-4	Ib	TMS	CH ₃ , H, CH ₃
Ib-5	Ib	iPr	CF ₃
Ib-6	Ib	tBu	CF ₃
Ib-7	Ib	iPr	DIP
Ic-1	Ic	iPr	CH ₃ , H, CH ₃
Ic-2	Ic	sBu	CH ₃ , H, CH ₃
Ic-3	Ic	tBu	CH ₃ , H, CH ₃
Ic-4	Ic	TMS	CH ₃ , H, CH ₃

lc-5	lc	iPr	CF ₃
lc-6	lc	tBu	CF ₃
lc-7	lc	iPr	DIP

iPr stand for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, DIP for 2,6-diisopropylphenyl.

The synthesis for some of the compound of general formula (I) is described for example by Z.

- 5 Yang in the Journal of the American Chemical Society, volume 138 (2016), page 2548-2551 or by S. Harder in Chemical Communications, volume 47 (2011), page 11945-11947 or by N. Kuhn in Zeitschrift für Anorganische und Allgemeine Chemie, volume 626 (2000) page 1387-1392.
- 10 Preferably, the central R' in the compound of general formula (II) is H. The compound of general formula (II) comprises the following general formulae.



- 15 Preferred examples for the compound of general formula (II) with reference to these general formulae are given in the following table.

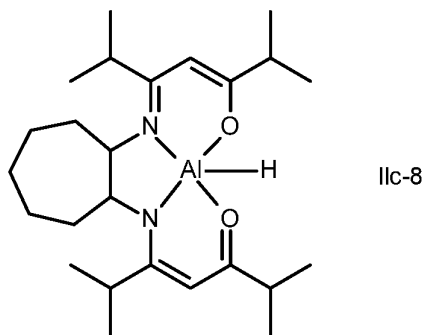
No.	Formula	R	R'
IIa-1	IIa	iPr	CH ₃ , H, CH ₃
IIa-2	IIa	sBu	CH ₃ , H, CH ₃
IIa-3	IIa	tBu	CH ₃ , H, CH ₃
IIa-4	IIa	TMS	CH ₃ , H, CH ₃
IIa-5	IIa	iPr	CF ₃
IIa-6	IIa	tBu	CF ₃
IIa-7	IIa	iPr	DIP
IIb-1	IIb	iPr	CH ₃ , H, CH ₃
IIb-2	IIb	sBu	CH ₃ , H, CH ₃
IIb-3	IIb	tBu	CH ₃ , H, CH ₃
IIb-4	IIb	TMS	CH ₃ , H, CH ₃
IIb-5	IIb	iPr	CF ₃
IIb-6	IIb	tBu	CF ₃

IIb-7	IIb	iPr	DIP
IIc-1	IIc	iPr	CH ₃
IIc-2	IIc	sBu	CH ₃
IIc-3	IIc	tBu	CH ₃
IIc-4	IIc	TMS	CH ₃
IIc-5	IIc	iPr	CF ₃
IIc-6	IIc	tBu	CF ₃
IIc-7	IIc	iPr	DIP
IId-1	IId	iPr	CH ₃
IId-2	IId	sBu	CH ₃
IId-3	IId	tBu	CH ₃
IId-4	IId	TMS	CH ₃
IId-5	IId	iPr	CF ₃
IId-6	IId	tBu	CF ₃
IId-7	IId	iPr	DIP
IIf-1	IIf	-	CH ₃
IIf-2	IIf	-	CF ₃
IIf-3	IIf	-	DIP

iPr stand for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, DIP for 2,6-diisopropylphenyl.

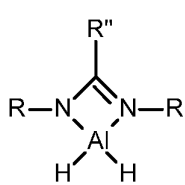
5 The synthesis for some of the compound of general formula (II) is described for example by P. Kuo in the European Journal of Inorganic Chemistry, volume 24 (2004), page 4898-4906.

An example for a compound in which two R form together a ring is the compound IIc-8 which is disclosed in KR 2016 / 116 180 A.

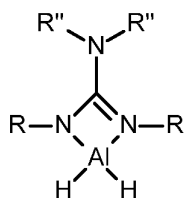


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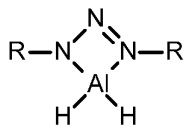
The compound of general formula (III) comprises the following general formulae.



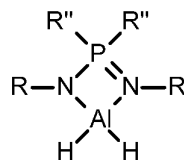
(IIIa)



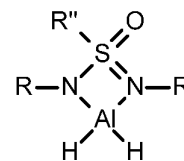
(IIIb)



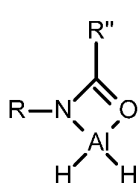
(IIIc)



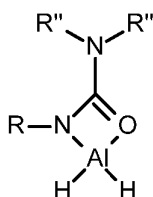
(IIIId)



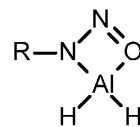
(IIIe)



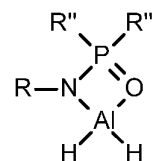
(IIIIf)



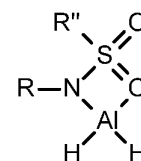
(IIIg)



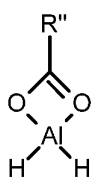
(IIIh)



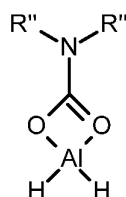
(IIIi)



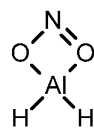
(IIIj)



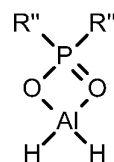
(IIIk)



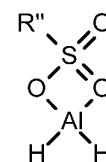
(IIIl)



(IIIm)



(IIIo)



(IIIp)

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Preferably, the compound of general formula (III) is a compound of general formula (IIIc), (IIIe), (IIIf), (IIIj), (IIIk), (IIIp), (IIIq). Preferred examples for the compound of general formula (III) with reference to these general formulae are given in the following table.

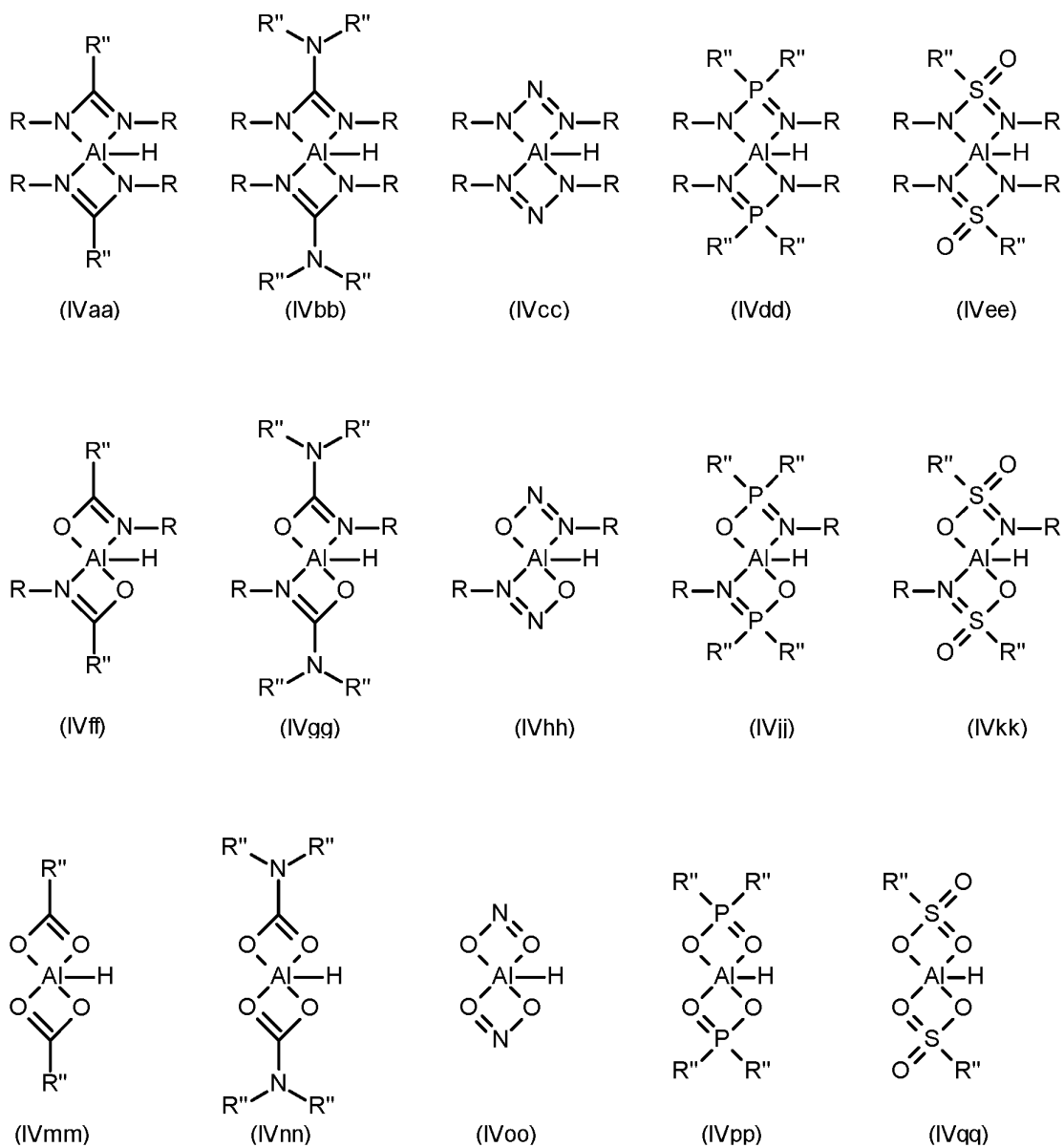
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No.	Formula	R	R''
IIIc-1	IIIc	iPr	-
IIIc-2	IIIc	sBu	-
IIIc-3	IIIc	tBu	-
IIIc-4	IIIc	TMS	-
IIIc-5	IIIc	DIP	-
IIIe-1	IIIe	iPr	CH ₃
IIIe-2	IIIe	sBu	CH ₃
IIIe-3	IIIe	tBu	CH ₃
IIIe-4	IIIe	TMS	CH ₃
IIIe-5	IIIe	DIP	CH ₃
IIIe-6	IIIe	tBu	Et
IIIe-7	IIIe	iPr	CF ₃
IIIe-8	IIIe	tBu	CF ₃
IIIe-9	IIIe	TMS	Ph

IIIe-10	IIIe	iPr	DIP
IIIf-1	IIIf	iPr	CH ₃
IIIf-2	IIIf	sBu	CH ₃
IIIf-3	IIIf	tBu	CH ₃
IIIf-4	IIIf	TMS	CH ₃
IIIf-5	IIIf	DIP	CH ₃
IIIf-6	IIIf	tBu	Et
IIIf-7	IIIf	iPr	CF ₃
IIIf-8	IIIf	tBu	CF ₃
IIIf-9	IIIf	TMS	Ph
IIIf-10	IIIf	iPr	DIP
IIIj-1	IIIj	iPr	CH ₃
IIIj-2	IIIj	sBu	CH ₃
IIIj-3	IIIj	tBu	CH ₃
IIIj-4	IIIj	TMS	CH ₃
IIIj-5	IIIj	DIP	CH ₃
IIIj-6	IIIj	tBu	Et
IIIj-7	IIIj	iPr	CF ₃
IIIj-8	IIIj	tBu	CF ₃
IIIj-9	IIIj	TMS	Ph
IIIj-10	IIIj	iPr	DIP
IIIIm-1	IIIIm	-	CH ₃
IIIIm-2	IIIIm	-	Et
IIIIm-3	IIIIm	-	CF ₃
IIIIm-4	IIIIm	-	Ph
IIIIm-5	IIIIm	-	DIP
IIIp-1	IIIp	-	CH ₃
IIIp-2	IIIp	-	Et
IIIp-3	IIIp	-	CF ₃
IIIp-4	IIIp	-	Ph
IIIp-5	IIIp	-	DIP
IIIq-1	IIIq	-	CH ₃
IIIq-2	IIIq	-	Et
IIIq-3	IIIq	-	CF ₃
IIIq-4	IIIq	-	Ph
IIIq-5	IIIq	-	DIP

Et stands for ethyl, iPr for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, Ph for phenyl, DIP for 2,6-diisopropylphenyl.

The compound of general formula (IV) comprises the following homoleptic general formulae.



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10 Preferably, the compound of general formula (IV) is a compound of general formula (IVcc), (IVee), (IVff), (IVjj), (IVmm), (IVpp), (IVqq).

Preferred examples for the compound of general formula (IV) with reference to these general formulae are given in the following table.

No.	Formula	R	R''
IIIcc-1	IIIcc	iPr	-
IIIcc-2	IIIcc	sBu	-
IIIcc-3	IIIcc	tBu	-
IIIcc-4	IIIcc	TMS	-
IIIcc-5	IIIcc	DIP	-

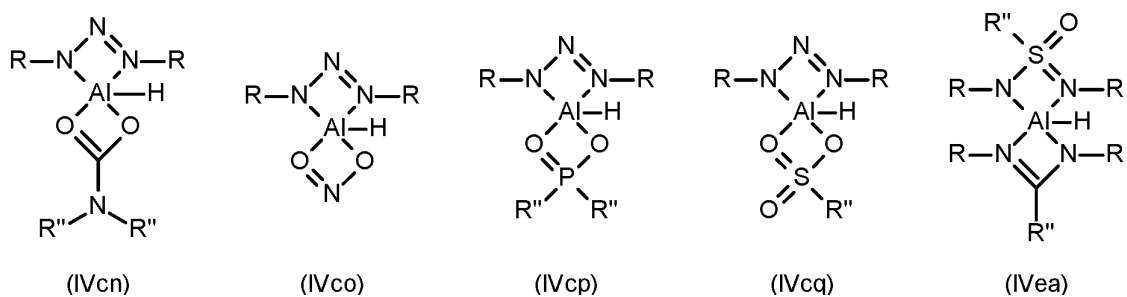
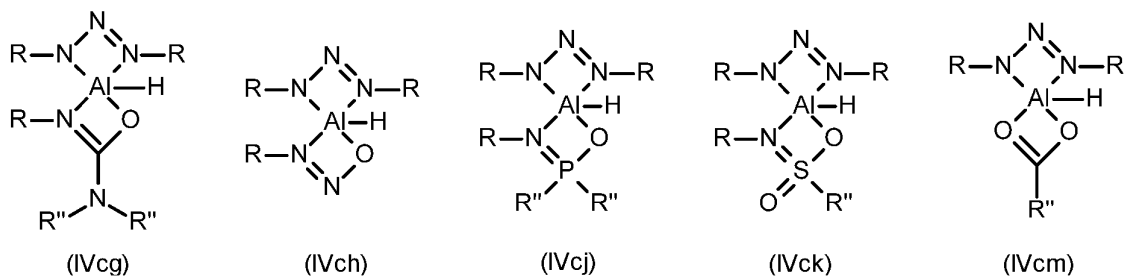
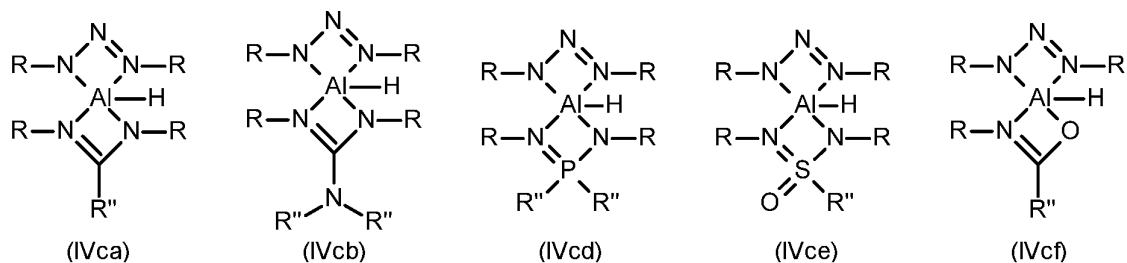
IIIee-1	IIIee	iPr	CH ₃
IIIee-2	IIIee	sBu	CH ₃
IIIee-3	IIIee	tBu	CH ₃
IIIee-4	IIIee	TMS	CH ₃
IIIee-5	IIIee	DIP	CH ₃
IIIee-6	IIIee	tBu	Et
IIIee-7	IIIee	iPr	CF ₃
IIIee-8	IIIee	tBu	CF ₃
IIIee-9	IIIee	TMS	Ph
IIIee-10	IIIee	iPr	DIP
IIIff-1	IIIff	iPr	CH ₃
IIIff-2	IIIff	sBu	CH ₃
IIIff-3	IIIff	tBu	CH ₃
IIIff-4	IIIff	TMS	CH ₃
IIIff-5	IIIff	DIP	CH ₃
IIIff-6	IIIff	tBu	Et
IIIff-7	IIIff	iPr	CF ₃
IIIff-8	IIIff	tBu	CF ₃
IIIff-9	IIIff	TMS	Ph
IIIff-10	IIIff	iPr	DIP
IIIjj-1	IIIjj	iPr	CH ₃
IIIjj-2	IIIjj	sBu	CH ₃
IIIjj-3	IIIjj	tBu	CH ₃
IIIjj-4	IIIjj	TMS	CH ₃
IIIjj-5	IIIjj	DIP	CH ₃
IIIjj-6	IIIjj	tBu	Et
IIIjj-7	IIIjj	iPr	CF ₃
IIIjj-8	IIIjj	tBu	CF ₃
IIIjj-9	IIIjj	TMS	Ph
IIIjj-10	IIIjj	iPr	DIP
IIImm-1	IIImm	-	CH ₃
IIImm-2	IIImm	-	Et
IIImm-3	IIImm	-	CF ₃
IIImm-4	IIImm	-	Ph
IIImm-5	IIImm	-	DIP
IIIpp-1	IIIpp	-	CH ₃
IIIpp-2	IIIpp	-	Et
IIIpp-3	IIIpp	-	CF ₃
IIIpp-4	IIIpp	-	Ph
IIIpp-5	IIIpp	-	DIP
IIIqq-1	IIIqq	-	CH ₃
IIIqq-2	IIIqq	-	Et

IIIqq-3	IIIqq	-	CF ₃
IIIqq-4	IIIqq	-	Ph
IIIqq-5	IIIqq	-	DIP

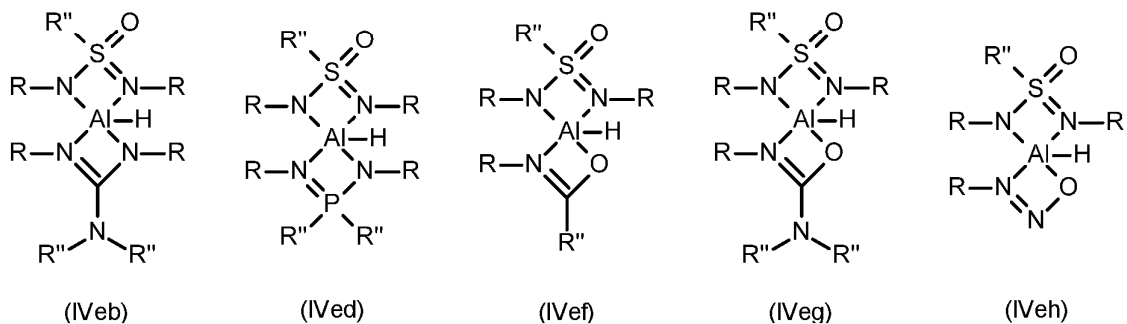
Et stands for ethyl, iPr for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, Ph for phenyl, DIP for 2,6-diisopropylphenyl.

Some preferred heteroelectronic compounds of general formula (IV) are shown below.

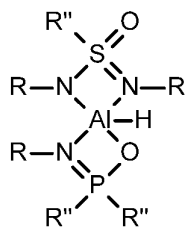
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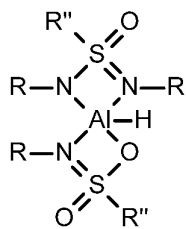
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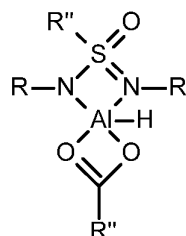
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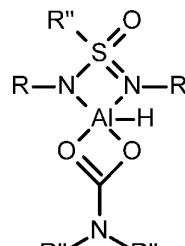
(IVej)



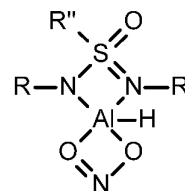
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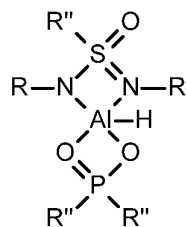
(IVem)



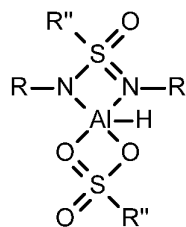
(IVen)



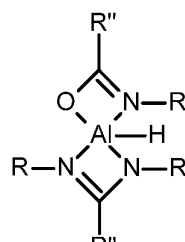
(IVeo)



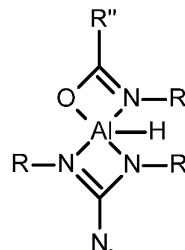
(IVep)



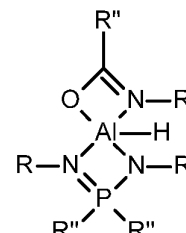
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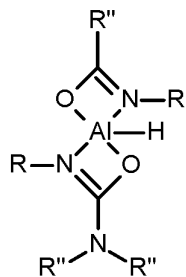
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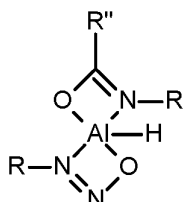
(IVfb)



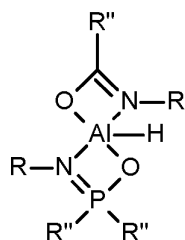
(IVfd)



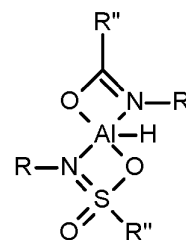
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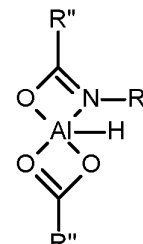
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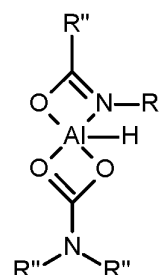
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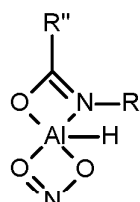
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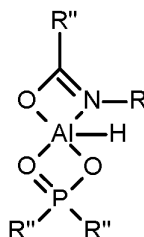
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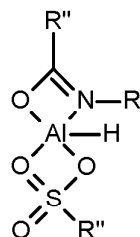
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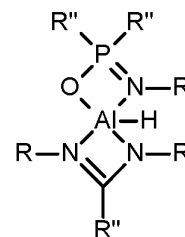
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(IVfp)

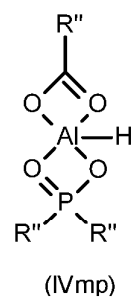
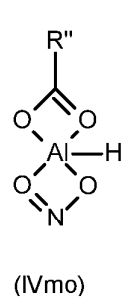
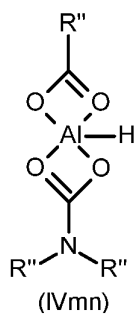
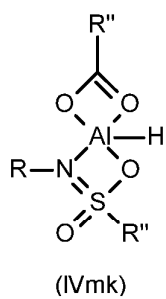
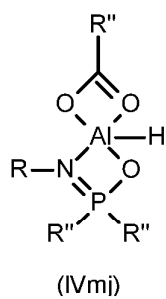
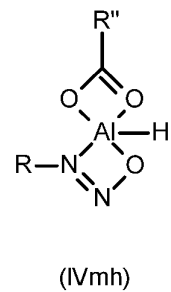
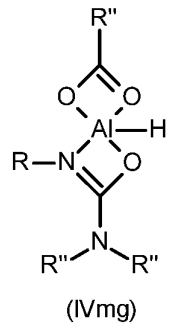
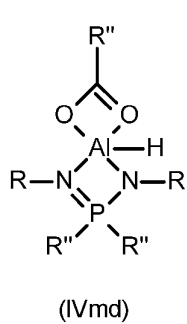
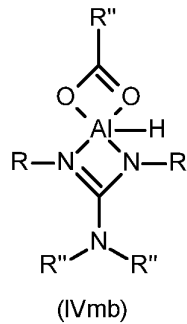
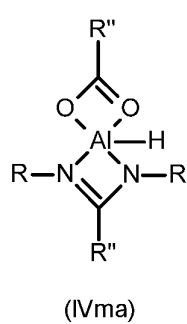
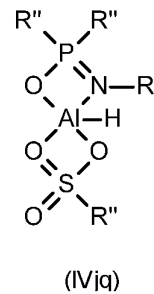
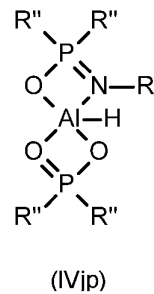
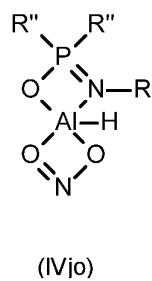
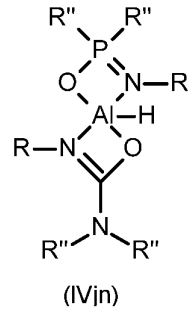
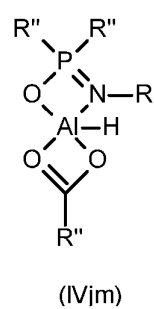
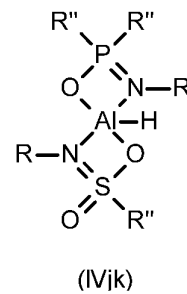
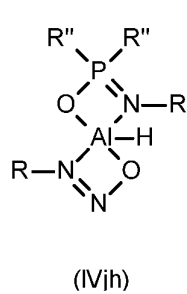
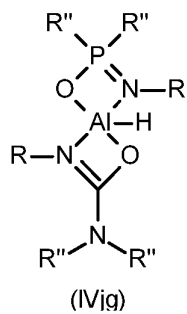
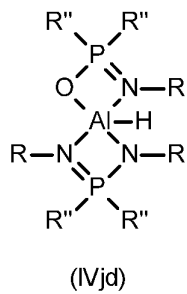
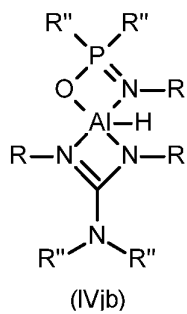


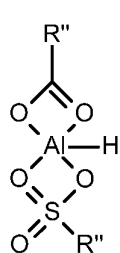
(IVfq)



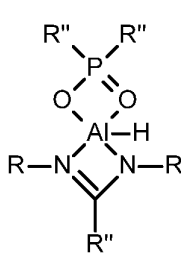
(IVia)

14

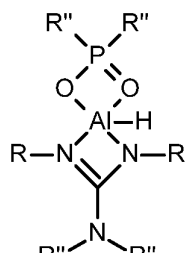




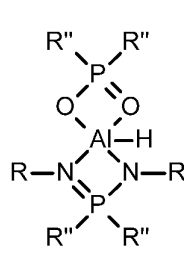
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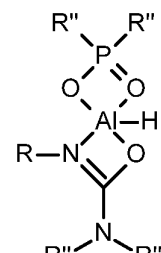
(IVpa)



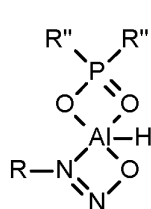
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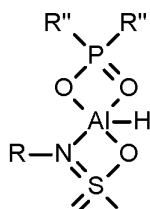
(IVpd)



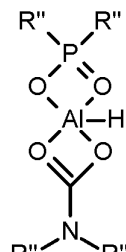
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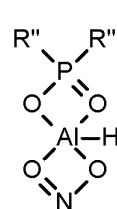
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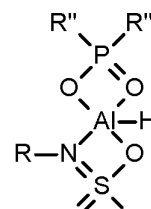
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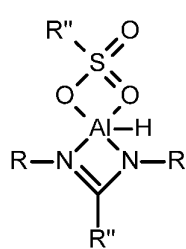
(IVpn)



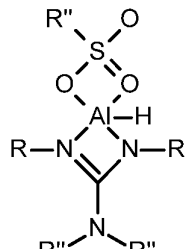
(IVpo)



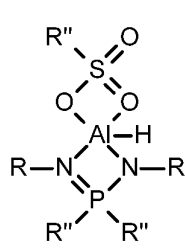
(IVpq)



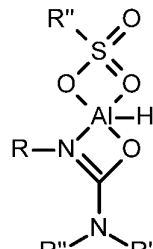
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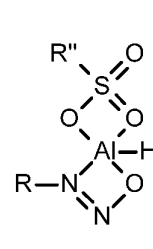
(IVqb)



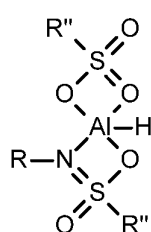
(IVqd)



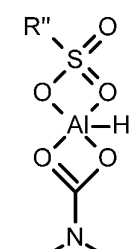
(IVqg)



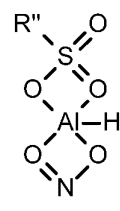
(IVqh)



(IVqk)



(IVqn)

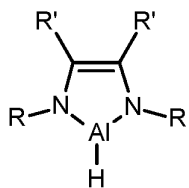


(IVqo)

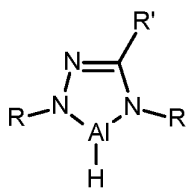
Particularly preferred heteroleptic compound of general formula (IV) are compounds of general formula (IVce), (IVcf), (IVcj), (IVcm), (IVcp), (IVcq), (IVef), (IVej), (IVem), (IVep), (IVeq), (IVfj), (IVfm), (IVfp), (IVfq), (IVjm), (IVjp), (IVjq), (IVpq).

The synthesis for some of the compound of general formula (IV) is described for example by A. Brazeau in Inorganic Chemistry, volume 45 (2006), page 2276-2281 or by B. Nekoueishahraki in Inorganic Chemistry, volume 48 (2009), page 9174-9179 or by R. Duchateau in Chemical Communications, volume 2 (1996), page 223-224 or by M. Cole in Zeitschrift für Anorganische und Allgemeine Chemie, volume 641 (2015), page 2233-2244.

The compound of general formula (V) comprises the following general formulae.



(Va)



(Vb)

5

Preferred examples for the compound of general formula (V) with reference to these general formulae are given in the following table.

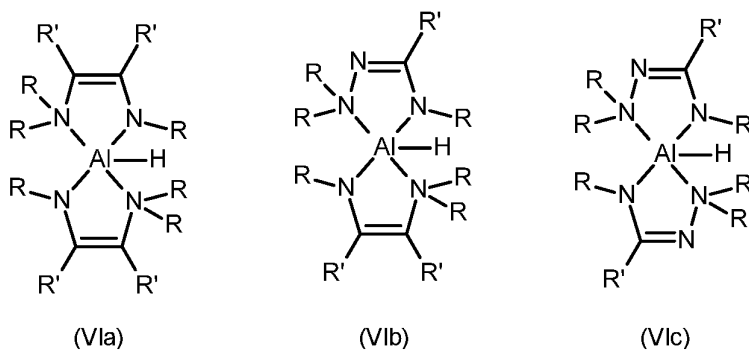
No.	Formula	R	R'
Va-1	Va	CH ₃	H
Va-2	Va	CH ₃	CH ₃
Va-3	Va	Et	CH ₃
Va-4	Va	iPr	CH ₃
Va-5	Va	sBu	CH ₃
Va-6	Va	tBu	CH ₃
Va-7	Va	TMS	CH ₃
Va-8	Va	Ph	CH ₃
Va-9	Va	DIP	CH ₃
Va-10	Va	CH ₃	Et
Va-11	Va	Et	Et
Va-12	Va	iPr	Et
Va-13	Va	tBu	Et
Va-14	Va	TMS	Et
Va-15	Va	Ph	Et
Va-16	Va	DIP	Et
Va-17	Va	TMS	Ph
Va-18	Va	tBu	H CH ₃
Va-19	Va	tBu	H Et
Va-20	Va	tBu	H Ph
Vb-1	Vb	CH ₃	H
Vb-2	Vb	CH ₃	CH ₃
Vb-3	Vb	Et	CH ₃
Vb-4	Vb	iPr	CH ₃
Vb-5	Vb	sBu	CH ₃

Vb-6	Vb	tBu	CH ₃
Vb-7	Vb	TMS	CH ₃
Vb-8	Vb	Ph	CH ₃
Vb-9	Vb	DIP	CH ₃
Vb-10	Vb	CH ₃	Et
Vb-11	Vb	Et	Et
Vb-12	Vb	iPr	Et
Vb-13	Vb	tBu	Et
Vb-14	Vb	TMS	Et
Vb-15	Vb	Ph	Et
Vb-16	Vb	DIP	Et
Vb-17	Vb	TMS	Ph
Vb-18	Vb	tBu	H CH ₃
Vb-19	Vb	tBu	H Et
Vb-20	Vb	tBu	H Ph

Et stands for ethyl, iPr for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, Ph for phenyl, DIP for 2,6-diisopropylphenyl.

The compound of general formula (VI) comprises the following general formulae.

5



Preferred examples for the compound of general formula (VI) with reference to these general formulae are given in the following table.

10

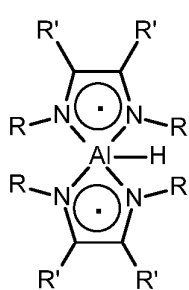
No.	Formula	R	R'
Vla-1	Vla	CH ₃	H
Vla-2	Vla	CH ₃	CH ₃
Vla-3	Vla	Et	CH ₃
Vla-4	Vla	iPr	CH ₃
Vla-5	Vla	sBu	CH ₃
Vla-6	Vla	tBu	CH ₃

Vla-7	Vla	TMS	CH ₃
Vla-8	Vla	Ph	CH ₃
Vla-9	Vla	DIP	CH ₃
Vla-10	Vla	CH ₃	Et
Vla-11	Vla	Et	Et
Vla-12	Vla	iPr	Et
Vla-13	Vla	tBu	Et
Vla-14	Vla	TMS	Et
Vla-15	Vla	Ph	Et
Vla-16	Vla	DIP	Et
Vla-17	Vla	TMS	Ph
Vla-18	Vla	tBu	H CH ₃
Vla-19	Vla	tBu	H Et
Vla-20	Vla	tBu	H Ph
Vlb-1	Vlb	CH ₃	H
Vlb-2	Vlb	CH ₃	CH ₃
Vlb-3	Vlb	Et	CH ₃
Vlb-4	Vlb	iPr	CH ₃
Vlb-5	Vlb	sBu	CH ₃
Vlb-6	Vlb	tBu	CH ₃
Vlb-7	Vlb	TMS	CH ₃
Vlb-8	Vlb	Ph	CH ₃
Vlb-9	Vlb	DIP	CH ₃
Vlb-10	Vlb	CH ₃	Et
Vlb-11	Vlb	Et	Et
Vlb-12	Vlb	iPr	Et
Vlb-13	Vlb	tBu	Et
Vlb-14	Vlb	TMS	Et
Vlb-15	Vlb	Ph	Et
Vlb-16	Vlb	DIP	Et
Vlb-17	Vlb	TMS	Ph
Vlb-18	Vlb	tBu	H CH ₃
Vlb-19	Vlb	tBu	H Et
Vlb-20	Vlb	tBu	H Ph
Vlc-1	Vlc	CH ₃	H
Vlc-2	Vlc	CH ₃	CH ₃
Vlc-3	Vlc	Et	CH ₃

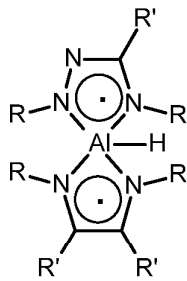
Vlc-4	Vlc	iPr	CH ₃
Vlc-5	Vlc	sBu	CH ₃
Vlc-6	Vlc	tBu	CH ₃
Vlc-7	Vlc	TMS	CH ₃
Vlc-8	Vlc	Ph	CH ₃
Vlc-9	Vlc	DIP	CH ₃
Vlc-10	Vlc	CH ₃	Et
Vlc-11	Vlc	Et	Et
Vlc-12	Vlc	iPr	Et
Vlc-13	Vlc	tBu	Et
Vlc-14	Vlc	TMS	Et
Vlc-15	Vlc	Ph	Et
Vlc-16	Vlc	DIP	Et
Vlc-17	Vlc	TMS	Ph
Vlc-18	Vlc	tBu	H CH ₃
Vlc-19	Vlc	tBu	H Et
Vlc-20	Vlc	tBu	H Ph

Et stands for ethyl, iPr for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, Ph for phenyl, DIP for 2,6-diisopropylphenyl.

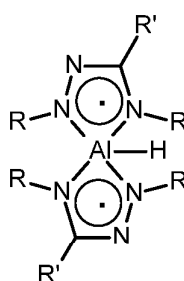
In the compound of general formula (VII), the central aluminum atom is bond to two radical monoanionic ligands which are derived from 1,4-diazabutadiene or 1,2,4-triazabutadiene. The compound of general formula (VII) comprises the following general formulae.



(VIIa)



(VIIb)



(VIIc)

Preferred examples for the compound of general formula (VII) with reference to these general formulae are given in the following table.

No.	Formula	R	R'
VIIa-1	VIIa	CH ₃	H
VIIa-2	VIIa	CH ₃	CH ₃

VIIa-3	VIIa	Et	CH ₃
VIIa-4	VIIa	iPr	CH ₃
VIIa-5	VIIa	sBu	CH ₃
VIIa-6	VIIa	tBu	CH ₃
VIIa-7	VIIa	TMS	CH ₃
VIIa-8	VIIa	Ph	CH ₃
VIIa-9	VIIa	DIP	CH ₃
VIIa-10	VIIa	CH ₃	Et
VIIa-11	VIIa	Et	Et
VIIa-12	VIIa	iPr	Et
VIIa-13	VIIa	tBu	Et
VIIa-14	VIIa	TMS	Et
VIIa-15	VIIa	Ph	Et
VIIa-16	VIIa	DIP	Et
VIIa-17	VIIa	TMS	Ph
VIIa-18	VIIa	tBu	H CH ₃
VIIa-19	VIIa	tBu	H Et
VIIa-20	VIIa	tBu	H Ph
VIIb-1	VIIb	CH ₃	H
VIIb-2	VIIb	CH ₃	CH ₃
VIIb-3	VIIb	Et	CH ₃
VIIb-4	VIIb	iPr	CH ₃
VIIb-5	VIIb	sBu	CH ₃
VIIb-6	VIIb	tBu	CH ₃
VIIb-7	VIIb	TMS	CH ₃
VIIb-8	VIIb	Ph	CH ₃
VIIb-9	VIIb	DIP	CH ₃
VIIb-10	VIIb	CH ₃	Et
VIIb-11	VIIb	Et	Et
VIIb-12	VIIb	iPr	Et
VIIb-13	VIIb	tBu	Et
VIIb-14	VIIb	TMS	Et
VIIb-15	VIIb	Ph	Et
VIIb-16	VIIb	DIP	Et
VIIb-17	VIIb	TMS	Ph
VIIb-18	VIIb	tBu	H CH ₃
VIIb-19	VIIb	tBu	H Et
VIIb-20	VIIb	tBu	H

			Ph
VIIc-1	VIIc	CH ₃	H
VIIc-2	VIIc	CH ₃	CH ₃
VIIc-3	VIIc	Et	CH ₃
VIIc-4	VIIc	iPr	CH ₃
VIIc-5	VIIc	sBu	CH ₃
VIIc-6	VIIc	tBu	CH ₃
VIIc-7	VIIc	TMS	CH ₃
VIIc-8	VIIc	Ph	CH ₃
VIIc-9	VIIc	DIP	CH ₃
VIIc-10	VIIc	CH ₃	Et
VIIc-11	VIIc	Et	Et
VIIc-12	VIIc	iPr	Et
VIIc-13	VIIc	tBu	Et
VIIc-14	VIIc	TMS	Et
VIIc-15	VIIc	Ph	Et
VIIc-16	VIIc	DIP	Et
VIIc-17	VIIc	TMS	Ph
VIIc-18	VIIc	tBu	H CH ₃
VIIc-19	VIIc	tBu	H Et
VIIc-20	VIIc	tBu	H Ph

Et stands for ethyl, iPr for iso-propyl, sBu for sec-butyl, tBu for tert-butyl, TMS for trimethylsilyl, Ph for phenyl, DIP for 2,6-diisopropylphenyl.

- Preferably, R bears no hydrogen atom in the 1-position, i.e. R bears no hydrogen atom which is bonded to the atom which is bonded to the nitrogen or oxygen atom, which is thus in the beta-position with regard to the aluminum atom. Also preferably, R'' bears no hydrogen atom in the 1-position. More preferably, both R and R'' bear no hydrogen in the 1-position. Examples are alkyl group bearing two alkyl side groups in the 1-position, i.e. 1,1-dialkylalkyl, such as tert-butyl, 1,1-dimethylpropyl; alkyl groups with two halogens in the 1-position such as trifluoromethyl, trichloromethyl, 1,1-difluoroethyl; trialkylsilyl groups such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl; aryl groups, in particular phenyl or alkyl-substituted phenyl such as 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl. Alkyl groups bearing no hydrogen atom in the 1-position are particularly preferred.
- The compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) preferably has a molecular weight of not more than 1000 g/mol, more preferably not more than 800 g/mol, even more preferably not more than 600 g/mol, in particular not more than 500 g/mol.

Preferably, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) has a melting point ranging from -80 to 125 °C, preferably from -60 to 80 °C, even more preferably from -40 to 50 °C, in particular from -20 to 20°C. It is advantageous if the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) melts to give a clear liquid which remains unchanged until a decomposition temperature.

Preferably, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) has a decomposition temperature of at least 80 °C, more preferably at least 100 °C, in particular at least 120 °C, such as at least 150 °C. Often, the decomposition temperature is not more than 250 °C. The compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) has a high vapor pressure. Preferably, the vapor pressure is at least 1 mbar at a temperature of 200 °C, more preferably at 150 °C, in particular at 120 °C. Usually, the temperature at which the vapor pressure is 1 mbar is at least 50 °C.

The compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) used in the process according to the present invention are used at high purity to achieve the best results. High purity means that the substance used contains at least 90 wt.-% metal- or semimetal-containing compound or compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII), preferably at least 95 wt.-%, more preferably at least 98 wt.-%, in particular at least 99 wt.-%. The purity can be determined by elemental analysis according to DIN 51721 (Prüfung fester Brennstoffe - Bestimmung des Gehaltes an Kohlenstoff und Wasserstoff - Verfahren nach Radmacher-Hoverath, August 2001).

The compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is brought in contact with the solid substrate from the gaseous state. It can be brought into the gaseous state for example by heating them to elevated temperatures. In any case a temperature below the decomposition temperature of the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) has to be chosen. The decomposition temperature is the temperature at which the pristine compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) begins changing its chemical structure and composition. Preferably, the heating temperature ranges from 0 °C to 300 °C, more preferably from 10 °C to 250 °C, even more preferably from 20 °C to 200 °C, in particular from 30 °C to 150 °C.

Another way of bringing the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) into the gaseous state is direct liquid injection (DLI) as described for example in US 2009 / 0 226 612 A1. In this method the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is typically dissolved in a solvent and sprayed in a carrier gas or vacuum. If the vapor pressure of the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) and the temperature are sufficiently high and the pressure is sufficiently low the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is brought into the gaseous state. Various solvents can be used provided that the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) shows sufficient solubility in that solvent such as at least 1 g/l, preferably at least 10 g/l, more preferably at least 100

g/l. Examples for these solvents are coordinating solvents such as tetrahydrofuran, dioxane, diethoxyethane, pyridine or non-coordinating solvents such as hexane, heptane, benzene, toluene, or xylene. Solvent mixtures are also suitable.

- 5 Alternatively, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) can be brought into the gaseous state by direct liquid evaporation (DLE) as described for example by J. Yang et al. (Journal of Materials Chemistry, 2015). In this method, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is mixed with a solvent, for example a hydrocarbon such as tetradecane, and heated below the boiling point of the solvent. By evaporation of the solvent, the
10 compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is brought into the gaseous state. This method has the advantage that no particulate contaminants are formed on the surface.

- 15 It is preferred to bring the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) into the gaseous state at decreased pressure. In this way, the process can usually be performed at lower heating temperatures leading to decreased decomposition of the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII). It is also possible to use increased pressure to push the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) in the gaseous state towards the solid substrate. Often, an inert gas, such as nitrogen or argon, is used as carrier gas
20 for this purpose. Preferably, the pressure is 10 bar to 10^{-7} mbar, more preferably 1 bar to 10^{-3} mbar, in particular 1 to 0.01 mbar, such as 0.1 mbar.

- Typically, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) acts as reducing agent in the process. According to the present invention a metal- or semimetal-containing compound is deposited from the gaseous state onto the solid substrate before bringing it in contact
25 with a compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII). The metal- or semimetal-containing compound is usually reduced to a metal, a metal nitride, a metal carbide, a metal carbonitride, a metal alloy, an intermetallic compound or mixtures thereof. Metal films in the context of the present invention are metal- or semimetal-containing films with high electrical
30 conductivity, usually at least 10^4 S/m, preferably at least 10^5 S/m, in particular at least 10^6 S/m.

- The compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) has a low tendency to form a permanent bond with the surface of the solid substrate with the deposited metal- or semimetal-containing compound. As a result, the metal- or semimetal-containing film hardly gets
35 contaminated with the reaction by-products of the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII). Preferably, the metal- or semimetal-containing film contains in sum less than 5 weight-% nitrogen, more preferably less than 1 wt.-%, in particular less than 0.5 wt.-%, such as less than 0.2 wt.-%.

- 40 The metal- or semimetal-containing compound contains at least one metal or semimetal atom. Metals include Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Bi. Semimetals include B, Si, Ge, As, Sb, Se, Te. Preferably, the metal- or semimetal-containing compound contains a metal or semimetal

which is more electropositive than Cu, more preferably more electropositive than Ni. In particular, the metal- or semimetal-containing compound contains Ti, Ta, Mn, Mo, W, Ge, Ga, As, In, Sb, Te, Al or Si. It is possible that more than one metal- or semimetal-containing compound is deposited on the surface, either simultaneously or consecutively. If more than one metal- or semimetal-containing compound is deposited on a solid substrate it is possible that all metal- or semimetal-containing compounds contain the same metal or semimetals or different ones, preferably they contain different metals or semimetals.

Any metal- or semimetal-containing compound, which can be brought into the gaseous state, is suitable. These compounds include metal or semimetal alkyls such as dimethyl zinc, trimethylaluminum; metal alkoxylates such as tetramethoxy silicon, tetra-isopropoxy zirconium or tetra-isopropoxy titanium; metal or semimetal cyclopentadienyl complexes like pentamethylcyclopentadienyl-trimethoxy titanium or di(ethylcyclopentadienyl) manganese; metal or semimetal carbenes such as tris(neopentyl)neopentylidene tantalum or bisimidazolidinyliden ruthenium chloride; metal or semimetal halides such as aluminum trichloride, tantalum pentachloride, titanium tetrachloride, molybdenum pentachloride, germanium tetrachloride, gallium trichloride, arsenic trichloride or tungsten hexachloride; carbon monoxide complexes like hexacarbonyl chromium or tetracarbonyl nickel; amine complexes such as bis(tert-butylimino)bis(dimethylamino)molybdenum, bis(tert-butylimino)bis(dimethylamino)tungsten or tetrakis(dimethylamino)titanium; diketone complexes such as tris(acetylacetonato)aluminum or bis(2,2,6,6-tetramethyl-3,5-heptanedionato) manganese. Metal or semimetal halides are preferred, in particular aluminum chloride, aluminum bromide and aluminum iodide. It is preferred that the molecular weight of the metal- or semimetal-containing compound is up to 1000 g/mol, more preferred up to 800 g/mol, in particular up to 600 g/mol, such as up to 500 g/mol.

The process is preferably performed as atomic layer deposition (ALD) process. Preferably, the sequence comprising (a) and (b) is performed at least twice, more preferably at least five times, even more preferably at least 10 times, in particular at least 50 times. Often, the sequence comprising (a) and (b) is performed not more than 1000 times.

Generally, it is preferred to purge the substrate and its surrounding apparatus with an inert gas each time the solid substrate is exposed to the metal- or semimetal-containing compound or the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) in the gaseous state. Preferred examples for inert gases are nitrogen and argon. Purging can take 1 s to 1 min, preferably 5 to 30 s, more preferably from 10 to 25 s, in particular 15 to 20 s.

Preferably, the temperature of the substrate is 5 °C to 40 °C higher than the place where the metal- or semimetal-containing compound is brought into the gaseous state, for example 20 °C. Preferably, the temperature of the substrate is from room temperature to 400 °C, more preferably from 100 to 300 °C, such as 150 to 220 °C.

Preferably, after deposition of a metal- or semimetal-containing compound on the solid substrate and before bringing the solid substrate with the deposited metal- or semimetal-containing compound in contact with the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII),

the solid substrate with the deposited metal- or semimetal-containing compound is brought in contact with an acid in the gaseous phase. Without being bound by a theory, it is believed that the protonation of the ligands of the metal- or semimetal-containing compound facilitates its decomposition and reduction. Suitable acids include hydrochloric acid and carboxylic acids, preferably, carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, or trifluoroacetic acid, in particular formic acid.

Alternatively, it is possible to deposit aluminum from the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII). In this case, the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) adsorbs to the surface of the solid substrate, for example because there are reactive groups such as OH groups on the surface of the solid substrate or the temperature of the solid substrate is sufficiently high. Preferably the adsorbed compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is decomposed.

The decomposition can be effected in various ways. The temperature of the solid substrate can be increased above the decomposition temperature. In this case, the process is a chemical vapor deposition (CVD) process. Typically, the solid substrate is heated to a temperature in the range of 300 to 1000 °C, preferably in the range of 350 to 600 °C.

Furthermore, it is possible to expose the deposited compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) to a plasma like an oxygen plasma, hydrogen plasma, ammonia plasma, or nitrogen plasma; to oxidants like oxygen, oxygen radicals, ozone, nitrous oxide (N₂O), nitric oxide (NO), nitrogendioxide (NO₂) or hydrogenperoxide; to ammonia or ammonia derivatives for example tert-butylamine, iso-propylamine, dimethylamine, methylethylamine, or diethylamine; to hydrazine or hydrazine derivatives like N,N-dimethylhydrazine; to solvents like water, alkanes, or tetrachlorocarbon; or to boron compound like borane. The choice depends on the chemical structure of the desired layer. For aluminum oxide, it is preferable to use oxidants, plasma or water, in particular oxygen, water, oxygen plasma or ozone. For aluminum, nitride, ammonia, hydrazine, hydrazine derivatives, nitrogen plasma or ammonia plasma are preferred. For aluminum boride boron compounds are preferred. For aluminum carbide, alkanes or tetrachlorocarbon are preferred. For aluminum carbide nitride, mixtures including alkanes, tetrachlorocarbon, ammonia and/or hydrazine are preferred.

The process is preferably performed as atomic layer deposition (ALD) process comprising the sequence

(c) bringing a solid substrate in contact with a compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) and

(d) decomposing the adsorbed compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII). Preferably, the sequence comprising (c) and (d) is performed at least twice, more preferably at least five times, even more preferably at least 10 times, in particular at least 50 times. Often, the sequence comprising (c) and (d) is performed not more than 1000 times.

In this case the temperature of the substrate is preferably 5 °C to 40 °C higher than the place where the metal- or semimetal-containing compound is brought into the gaseous state, for example 20 °C. Preferably, the temperature of the substrate is from room temperature to 400 °C, more preferably from 100 to 300 °C, such as 150 to 220 °C.

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If the temperature of the substrate in the process according to the present invention is kept below the decomposition temperature of the metal- or semimetal-containing compound, typically a monolayer is deposited on the solid substrate. Once a molecule of the metal- or semimetal-containing compound is deposited on the solid substrate further deposition on top of it usually becomes less likely. Thus, the deposition of the metal- or semimetal-containing compound on the solid substrate preferably represents a self-limiting process step. The typical layer thickness of a self-limiting deposition processes step is from 0.01 to 1 nm, preferably from 0.02 to 0.5 nm, more preferably from 0.03 to 0.4 nm, in particular from 0.05 to 0.2 nm. The layer thickness is typically measured by ellipsometry as described in PAS 1022 DE (Referenzverfahren zur Bestimmung von optischen und dielektrischen Materialeigenschaften sowie der Schichtdicke dünner Schichten mittels Ellipsometrie; February 2004).

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The exposure of the substrate with the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) or the metal- or semimetal-containing compound can take from milliseconds to several minutes, preferably from 0.1 second to 1 minute, in particular from 1 to 10 seconds. The longer the solid substrate at a temperature below the decomposition temperature of the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) or the metal- or semimetal-containing compound is exposed to the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) or the metal- or semimetal-containing compound the more regular films formed with less defects.

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A particular advantage of the process according to the present invention is that the compound of general formula (I), (II), (III), (IV), (V), (VI), or (VII) is very versatile, so the process parameters can be varied in a broad range. Therefore, the process according to the present invention includes both a CVD process as well as an ALD process.

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The process according to the present invention yields an inorganic metal- or semimetal-containing film. A film can be only one monolayer of a metal or be thicker such as 0.1 nm to 1 µm, preferably 0.5 to 50 nm. A film can contain defects like holes. These defects, however, generally constitute less than half of the surface area covered by the film. The film preferably has a very uniform film thickness which means that the film thickness at different places on the substrate varies very little, usually less than 10 %, preferably less than 5 %. Furthermore, the film is preferably a conformal film on the surface of the substrate. Suitable methods to determine the film thickness and uniformity are XPS or ellipsometry.

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The film obtained by the process according to the present invention can be used in an electronic element. Electronic elements can have structural features of various sizes, for example from 1 nm to 100 µm, for example 10 nm, 14 nm or 22 nm. The process for forming the films for the electronic elements is particularly well suited for very fine structures. Therefore, electronic elements with sizes below 1 µm are preferred. Examples for electronic elements are field-effect

transistors (FET), solar cells, light emitting diodes, sensors, or capacitors. In optical devices such as light emitting diodes or light sensors the film obtained by the process according to the present invention serves to increase the refractive index of the layer which reflects light.

- 5 Preferred electronic elements are transistors. Preferably the film acts as chemical barrier metal in a transistor. A chemical barrier metal is a material which reduces diffusion of adjacent layers while maintaining electrical connectivity.

Examples

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Example 1a: Synthesis of 4-(isopropylamino) pent-3-en-2-one (ⁱPrNacacH)

A solution of 2,4-pentanedione (10.4 mL, 0.1 mol) in 100 mL of ethanol was added dropwise into a solution of isopropylamine (8.7 mL, 0.1 mol) in 100 mL of ethanol. The resultant pale yellow solution was refluxed at 100 °C for 18 h in a 250 mL round bottomed flask. The intense yellow colored solution was reduced in volume under reduced pressure. Fractional distillation of the residue at 78 °C under reduced pressure (0.8 Torr) afforded ⁱPrNacacH (11.859 g, 84% yield) as a pale-yellow liquid.

20 ¹H NMR (400 MHz, C₆D₆) δ = 0.82 (d, 6H), 1.51 (s, 3H), 1.96 (s, 3H), 3.19 (m, 1H), 4.83 (s, 1H), 11.10 (s, 1H). ¹³C{¹H} NMR (100 MHz, C₆D₆) δ = 18.59, 24.07, 29.23, 44.69, 95.47, 161.17, 194.26.

Example 1b: Synthesis of N, N'-Diisopropyl-2,4-pentanediketimine (ⁱPrNacNacH)

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A solution of ⁱPrNacacH (5.376 g, 0.038 mol) in dimethyl sulfate (6 mL, 0.063 mol) was stirred for 5 minutes at ambient temperature and was then allowed to stand for 24 h, affording a viscous, orange colored solution. Subsequent addition of excess isopropylamine (7 mL, 0.081 mol) and stirring for 1 h at ambient temperature increased the color intensity of the solution. A mixture of excess sodium methoxide in methanol (11 mL, 0.048 mol) was added and the mixture was stirred for 1 h at ambient temperature. The volatile components were evaporated under reduced pressure, and then water (40 mL) was added to the resultant product. The flask contents were transferred to a separatory funnel. The crude product was extracted with pentane (10 × 40 mL) and the combined organic fractions were dried over anhydrous Na₂SO₄. The solution was filtered through fluted filter paper to afford a clear solution. The volatile components were removed under reduced pressure to afford ⁱPrNacNacH (2.195 g) as an orange oil.

30 ¹H NMR (400 MHz, C₆D₆) δ = 1.13 (d, 12H), 1.73 (s, 6H), 3.48 (m, 2H), 4.48 (s, 1H), 11.66 (s, 1H).

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¹³C{¹H} NMR (100 MHz, C₆D₆) δ = 19.16, 25.44, 47.35, 94.98, 158.33.

The crude product was used to synthesize the aluminum complex without further purification.

Example 1c: Synthesis of compound Ia-1

A solution of AlCl_3 (0.372 g, 2.8 mmol) in 30 mL of diethyl ether was cannulated into a stirred solution of LiAlH_4 (0.334 g, 8.4 mmol) in 30 mL of diethyl ether at 0 °C in an ice bath. The resultant cloudy solution was warmed to room temperature, stirred for 40 minutes, and then recooled to -30 °C. Then, a solution of $i\text{PrNaCH}$ (2.035 g, 11.16 mmol) in 40 mL of diethyl ether was added dropwise. The resultant mixture was stirred at ambient temperature for 18 h and was then filtered through a 2-cm plug of Celite on a coarse glass frit. The diethyl ether was evaporated from the filtrate under reduced pressure to collect the intense yellow colored, creamy product. The crude product was purified by sublimation at 50 °C under reduced pressure to afford compound Ia-1 as pale-yellow crystals (1.251 g, 53% yield). mp = 62-63 °C.

^1H NMR (400 MHz, C_6D_6) δ = 1.31 (d, 12H), 1.56 (s, 6H), 3.48 (m, 2H), 4.41 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) δ = 21.88, 23.12, 50.59, 97.73, 166.96.

The thermogravimetric analysis result is shown in figure 1.

Example 2a: Synthesis of 4-(sec-butylamino) pent-3-en-2-one ($^s\text{BuNacacH}$)

A solution of 2,4-pentanedione (10.4 mL, 0.1 mol) in 100 mL ethanol was added dropwise into a solution of sec-butylamine (10 mL, 0.1 mol) in 100 mL ethanol. The resultant pale yellow solution was refluxed at 100 °C for 18 h in a 250 mL round bottomed flask. The intense yellow colored solution was reduced in volume under reduced pressure. Fractional distillation of the residue at 97 °C at 0.8 Torr afforded $^s\text{BuNacacH}$ as a pale yellow liquid (14.332 g, 92.3% yield).

^1H NMR (400 MHz, C_6D_6) δ = 0.68 (t, 3H), 0.80 (d, 3H), 1.16 (m, 2H), 1.51 (s, 3H), 1.98 (s, 3H), 3.00 (m, 1H), 4.84 (s, 1H), 11.13 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) δ = 10.69, 18.86, 21.95, 29.23, 31.12, 50.35, 95.51, 161.63, 194.30.

Example 2b: Synthesis of N, N'-Di(sec-butyl)-2,4-pentanediketimine ($^s\text{BuNacNacH}$)

A solution of $^s\text{BuNacacH}$ (4.005 g, 0.026 mol) in dimethyl sulfate (4 mL, 0.043 mol) was stirred for 5 min at ambient temperature and was then allowed to stand for 24 h, affording a viscous, orange colored solution. Subsequently, excess sec-butylamine (6 mL, 0.059 mol) was added and the solution was stirred for an additional two hours at ambient temperature. A mixture of excess sodium methoxide in methanol (7.5 mL, 0.033 mol) was added and the mixture was stirred for one hour. The volatile components were evaporated under reduced pressure and water (20 mL) was added to the resultant product. The flask contents were transferred to a separatory funnel. The crude product was extracted with pentane (10 × 35 mL) and the combined organic fractions were dried over anhydrous Na_2SO_4 . The solution was filtered through a fluted paper

filter. The residual solvents were evaporated under reduced pressure to afford crude ^sBuNacNach (5.810 g). The crude product was distilled at 85-87 °C at 0.8 Torr to afford ^sBuNacNach as a pale-yellow liquid (2.405 g, 45% yield).

5 ¹H NMR (400 MHz, C₆D₆) δ = 0.90 (t, 6H), 1.07 (d, 6H), 1.46 (m, 4H), 1.73 (s, 6H), 3.27 (m, 2H), 4.45 (s, 1H), 11.52 (s, 1H).

¹³C{¹H} NMR (100 MHz, C₆D₆) δ = 11.15, 19.43, 23.04, 32.54, 52.98, 95.16, 158.67.

10 Example 2c: Synthesis of compound Ia-2

A solution of AlCl₃ (0.381 g, 2.85 mmol) in 30 mL of diethyl ether was cannulated into a stirred solution of LiAlH₄ (0.343 g, 8.57 mmol) in 30 mL of diethyl ether at 0 °C in an ice bath. The resultant cloudy solution was warmed to room temperature, stirred for 40 minutes, and then
15 recooled to -30 °C. Then, a solution of ^sBuNacNach (2.405 g, 11.43 mmol) in 40 mL of diethyl ether was added dropwise. The resultant mixture was stirred at ambient temperature for 18 h and was then filtered through a 2-cm plug of Celite on a coarse glass frit. The diethyl ether was evaporated from the filtrate under reduced pressure to collect the yellow colored, creamy product. The crude product was purified by sublimation at 45 °C at 0.8 Torr to afford compound Ia-2
20 as pale-yellow crystals (0.967 g, 35.5 % yield). mp = 40 °C.

¹H NMR (400 MHz, C₆D₆) δ = 0.83 (6H, 2 CH(CH₃) CH₂CH₃), 1.32 (6H, 2 CH(CH₃) CH₂CH₃), 1.59 (8H, 2 β-C (CH₃) + 2 CH(CH₃)CHH'CH₃), 2.00 (2H, 2 CH(CH₃)CHH'CH₃), 3.23 (2H, CH (CH₃)CH₂CH₃), 4.50 (1H, α-CH).

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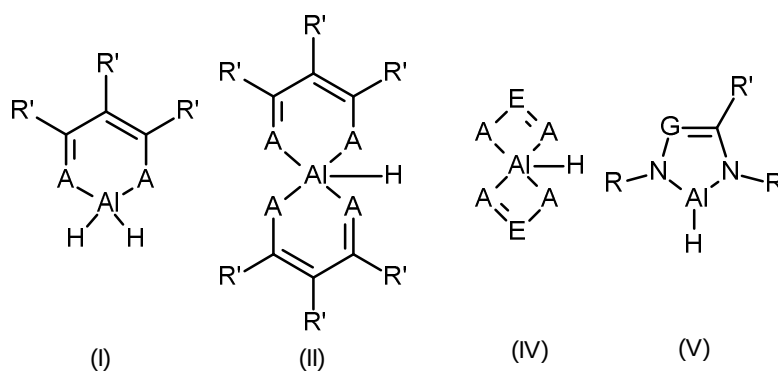
¹³C{¹H} NMR (100 MHz, C₆D₆) δ = 12.10, 21.54, 22.46, 30.43, 56.80, 97.91, 167.23.

The thermogravimetric analysis result is shown in figure 1.

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Claims

1. Process for preparing inorganic metal- or semimetal-containing films comprising
 - (a) depositing a metal- or semimetal-containing compound from the gaseous state onto a solid substrate and
 - (b) bringing the solid substrate in contact with a compound of general formula (I), (II), (IV), or (V) in the gaseous state



wherein A is NR or O,

E is CR'', CNR''₂, N, PR''₂, or SOR''

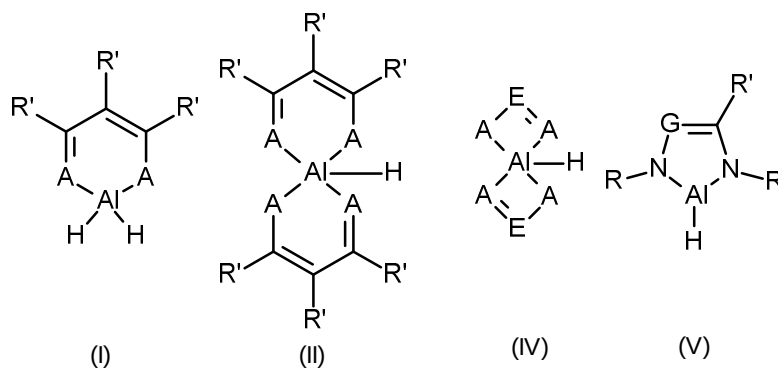
G is CR',

R is an alkyl group, an alkenyl group, an aryl group, or a silyl group and

R' and R'' are hydrogen, an alkyl group, an alkenyl group, an aryl group, or a silyl group, wherein the compound of general formula (I), (II), (IV), or (V) has a molecular weight of not more than 500 g/mol.

2. The process according to claim 1, wherein R is methyl, ethyl, iso-propyl, sec-butyl, tert-butyl, trimethylsilyl.
3. The process according to claim 1 or 2, wherein R bears no hydrogen atom in the 1-position.
4. The process according to any of the claims 1 to 3, wherein R' in the 3 position of the ligand in the compound of general formula (I) or (II) is H.
5. The process according to any of the claims 1 to 4, wherein the metal- or semimetal-containing compound contains Ti, Ta, Mn, Mo, W, Ge, Ga, As, In, Sb, Te, Al or Si.
6. The process according to any of the claims 1 to 5, wherein the metal- or semimetal-containing compound is a metal or semimetal halide.

7. The process according to any of the claims 1 to 6, wherein the sequence containing (a) and (b) is performed at least twice.
8. The process according to any of the claims 1 to 7, wherein the process is an atomic layer deposition process.
9. The process according to any of the claims 1 to 8, wherein the compound of general formula (I), (II), (IV), or (V) has a vapor pressure at least 1 mbar at a temperature of 200 °C.
10. The process according to any of the claims 1 to 9, wherein the compound of general formula (I), (II), (IV), or (V) has a melting point of -80 to 125 °C.
11. The process according to any of the claims 1 to 10, wherein the inorganic metal- or semi-metal-containing films contains less than 5 weight-% nitrogen.
12. Use of a compound of general formula (I), (II), (IV), or (V)



wherein A is NR or O,

E is CR'', CNR''₂, N, PR''₂, or SOR''

G is CR',

R is an alkyl group, an alkenyl group, an aryl group, or a silyl group and

R' and R'' are hydrogen, an alkyl group, an alkenyl group, an aryl group, or a silyl group,

wherein the compound of general formula (I), (II), (IV), or (V) has a molecular weight of

not more than 500 g/mol,

as reducing agent in a vapor deposition process.

13. Use according to claim 12, wherein the vapor deposition process is an atomic layer deposition process.