Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Aluminum nanoparticle preparation via catalytic decomposition of alane adducts – Influence of reaction parameters on nanoparticle size, morphology and reactivity

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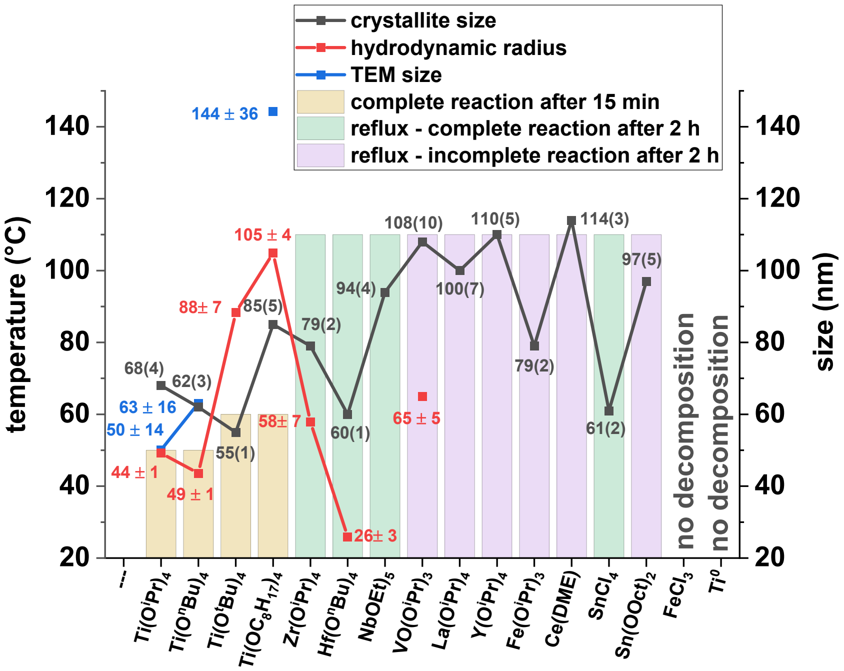


Figure S1: The concentrations used were as follows: 35 mM H_3AlNEt_3, Al: PPh_3 5:1 and cat.:Al 2 ppm. The crystallite sizes were determined from Rietveld refinements of the dried powders.

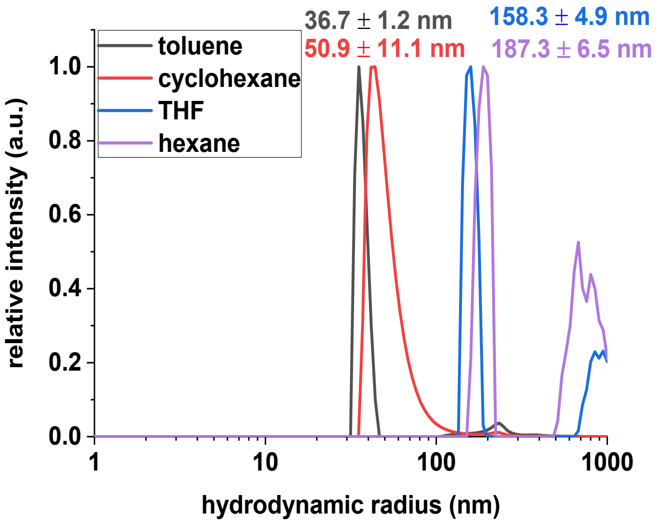
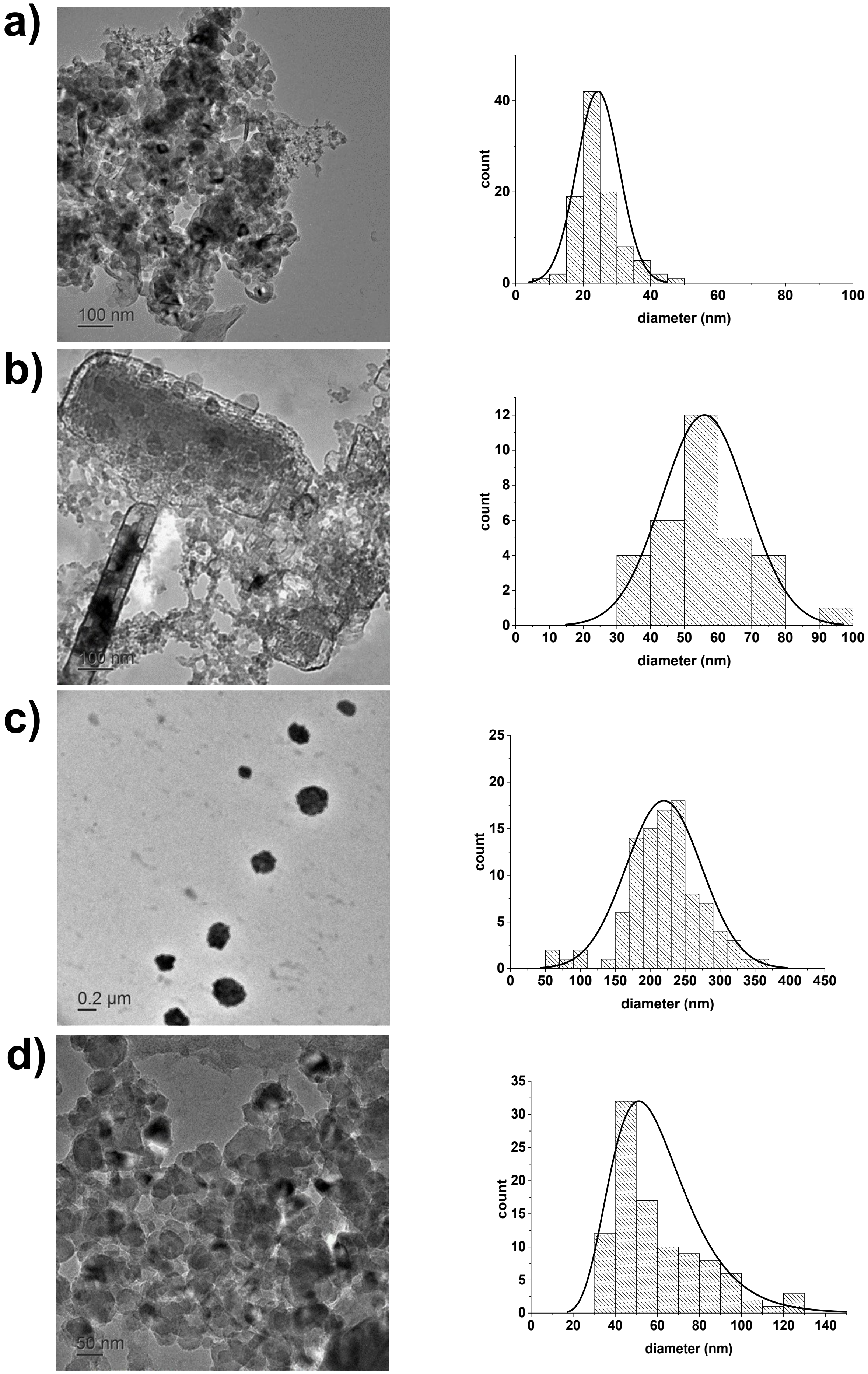


Figure S2: DLS measurements of Al nanoparticles synthesized from H_3AlNEt_3 in different solvents in methanol. The concentrations used were as follows: 35 mM H_3AlNEt_3, Al: epoxyhexane 4:1 and cat.:Al 2 ppm.


a)
100 nm
count
0
20
40
0
20
40
60
80
100
diameter (nm)
b)
100 nm
count
0
2
4
6
8
10
12
0
10
20
30
40
50
60
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diameter (nm)
c)
0.2 µm
count
0
5
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15
20
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diameter (nm)
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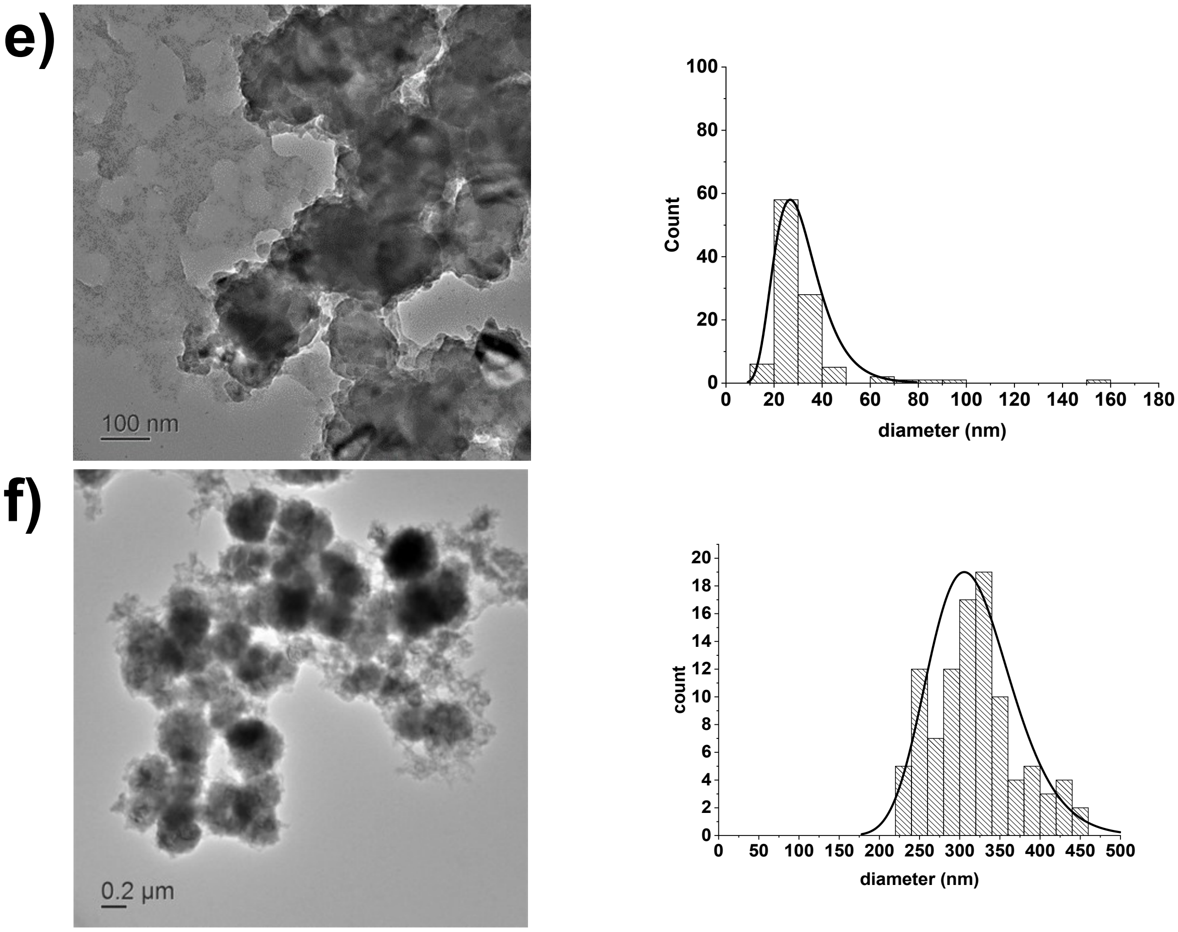


Figure S3: **a)** TEM image of Al particles synthesized from H_3AlNMe_2Et, **b)** H_3AlNBu_3, **c)** $H_3AlNOct_3$, **d)** $H_3Al{\cdot}THF$, **e)** $H_3Al{\cdot}IMes$, **f)** $H_3Al{\cdot}PCy_3$ and the respective particle size distributions

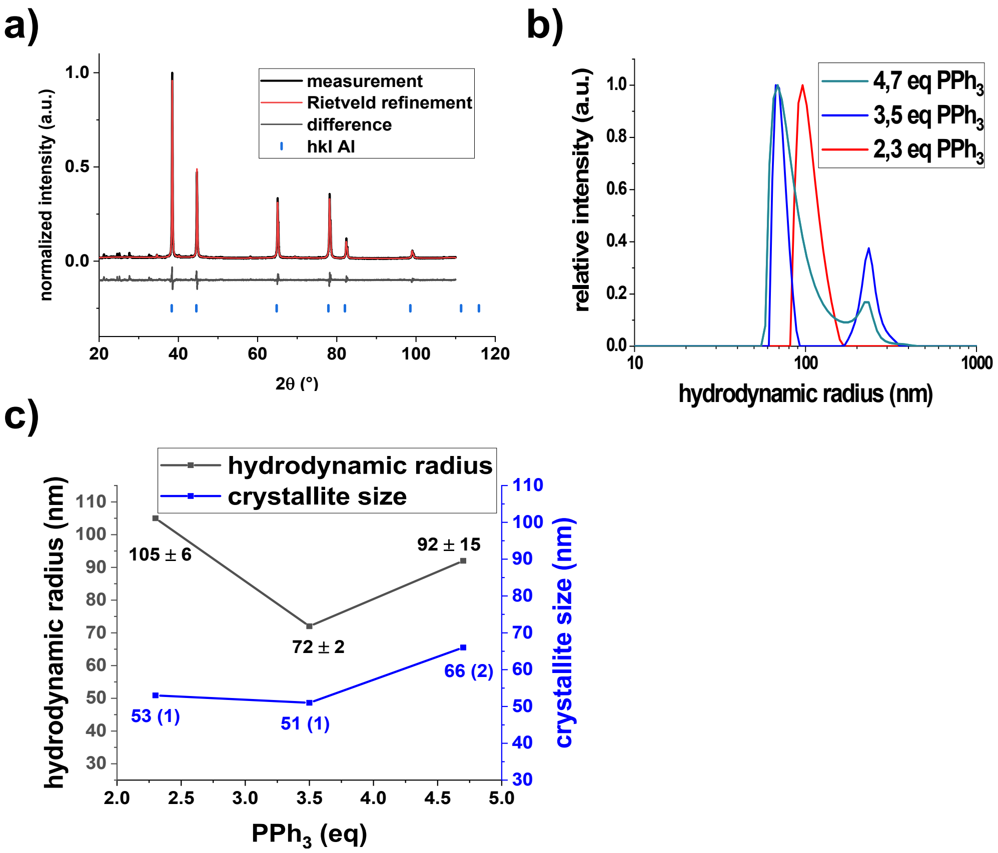


Figure S4: **a)** PXRD measurement and Rietveld refinement, **b)** DLS measurements in methanol, and **c)** a comparison of hydrodynamic radii as well as crystallite sizes of Al nanoparticles synthesized via a chemical reduction approach.

Table S1: CHN analyses of Al nanoparticles synthesized using different stabilizers in toluene. The concentrations used were as follows: 35 mM H_3AlNEt_3 (unless stated otherwise), and cat.:Al 2 ppm

stabilizer	C [%]	H[%]	N[%]	Σ (CHN) [%]
---	3.16	1.29	0.45	4.90
--- - $H_3AlNOct_3$ as precursor				
5.0 eq PPh_3	8.36	1.89	---	7.5
5.0 eq TOP	4.72	1.82	0.97	7.51
0.25 eq TOP				
5.0 eq $N(Oct)_3$	no decomposition			
0.25 eq $N(Oct)_3$	5.27	1.68	0.53	7.48
0.12 TOEDA	4.73	1.44	0.48	6.65
0.25 eq $N(Bu)_3$	2.82	0.95	0.33	4.10
0.25 eq NPh_3	3.01	1.01	0.50	4.52

0.25 eq $N(^iBu)_3$	4.74	1.63	0.53	6.90
0.25 eq TOPO	2.34	0.99	3.19	6.52
5.0 eq PCy_3				
5.0 eq NPh_3				

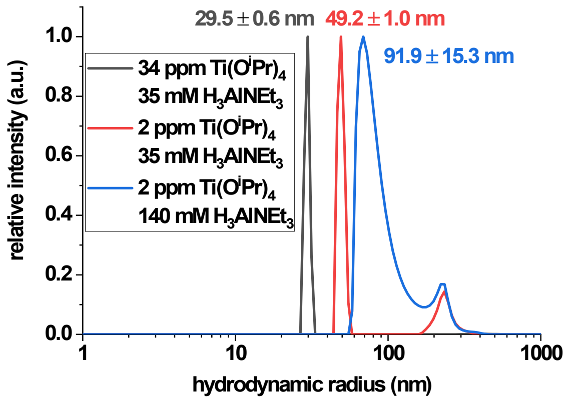


Figure S5: DLS measurements of Al nanoparticles synthesized in the presence of 5 eq. PPh_3 applying different concentrations of the precursor and decomposition catalyst.

Synthesis and characterization of the alane precursors

Methods

^1H, ^{13}C, ^{31}P and ^{27}Al NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. ^1H spectra were recorded at 400 MHz, ^{13}C at 101 MHz, ^{31}P at 162 MHz and ^{27}Al at 104 MHz. All spectra were recorded at room temperature in benzene-d$_6$ (C_6D_6) or chloroform-d ($CDCl_3$).

A Bruker Vertex 70 ATR-FTIR spectrometer was used for recording the IR spectra. The spectra were recorded as an average of 16 scans for background and sample in a range from 4000 – 400 cm^{-1} in a resolution of 4 cm^{-1} applying a DIAMOND ATR-QL measurement cell from Bruker in an atmosphere of flowing Ar.

A titriometric determination of the hydride content of the alane precursors was carried out according to methods described in the literature for $LiAlH_4$ [1,2]: The alane (~ 0.5 mmol) to be determined was dissolved in 10 ml of THF. To this solution 9-fluorenone was added dropwise (1 M in THF) under stirring until a yellow coloration remained visible.

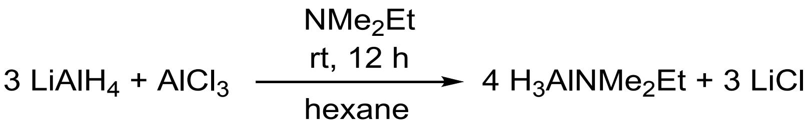
Materials

Tributylamine (NBu_3, >98 %) was purchased from TCI Japan (Tokyo, Japan) and trioctylamine ($N(Oct)_3$ < 92.5 %) was obtained from Merck (Darmstadt, Germany). Bis(2-dimethylaminoethyl)-methylamine (PMDTA, 99 %) and $LiAlH_4$ (95 %) were purchased from Sigma-Aldrich (Munich, Germany). Triethylamine (> 99 %) was purchased from applichem (Darmstadt, Germany). 1,4-Diazabicyclo[2.2.2]octane (DABCO, 98 %) was obtained from Alfa Aesar (Ward Hill, USA). $AlCl_3$ (98.5 %) was from Acros Organics (Geel, Belgium). Tricyclohexylphosphine (>97 %) was delivered from Carbosynth (Berkshire, United Kingdom). Toluene, THF, hexane, and diethylether were purified in a MBraun solvent purification system. All chemicals were used as received unless stated otherwise. The reactions were carried out under an Ar atmosphere using either a glove box or Schlenk line techniques.

Synthesis of H_3AlNR_3

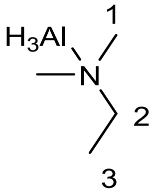
Triethylamine alane, tributylamine alane and trioctylamine alane were synthesized following known literature methods[3]. A typical synthesis was carried out as follows: 1.81 g $LiAlH_4$ (48 mmol) and 1.89 g $AlCl_3$ (14 mmol) were slurried in 50 ml of dry toluene. To this suspension 14.2 ml (60 mmol) tributylamine was added dropwise under stirring. The mixture was stirred over night at room temperature and filtered through a glass frit. The volume of the filtrate reduced to half of its volume and the resulting solution was stored at - 25 °C overnight. The resulting white solid was recrystallized from toluene and stored under Ar at - 25 °C. When Trioctylamine was used, no crystallization could be observed over a period of 3 months. Thus, the remaining solvent was removed in vacuo resulting in the formation of a colorless liquid, which was stored at -25 °C under Ar.

Yields: H_3AlNMe_2Et: colorless liquid, 5.4 g (85 % based on Al)
H_3AlNEt_3: colorless liquid, 24.7 g (76 % based on Al)
H_3AlNBu_3: white solid, 10.7 g (80 % based on Al)
$H_3AlNOct_3$: colorless liquid, yield could not be determined



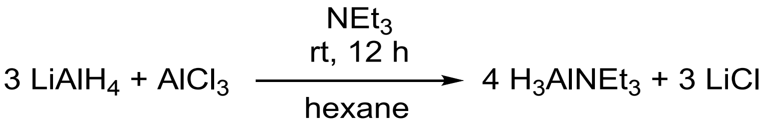
$$3\ LiAlH_4 + AlCl_3 \xrightarrow[\text{hexane}]{\text{NMe}_2\text{Et, rt, 12 h}} 4\ H_3AlNMe_2Et + 3\ LiCl$$

***Scheme S1**: Synthesis procedure for H_3AlNMe_2Et.*



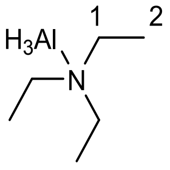
^{1}H NMR (C_6D_6; 400 MHz): 0.78 (tr; 3H; H3; J = 4 Hz), 1.94 (s; 6H; H1). 2.29 (q; 2H; H2; J = 8 Hz), 3.98 (br s; AlH) ppm. ^{13}C NMR (C_6D_6; 101 MHz): 9.18 (C3), 44.23 (C1), 53.93 (C2) ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 140.84 ppm.

H_3AlNEt_3



$$3\ LiAlH_4 + AlCl_3 \xrightarrow[\text{hexane}]{\text{NEt}_3\text{, rt, 12 h}} 4\ H_3AlNEt_3 + 3\ LiCl$$

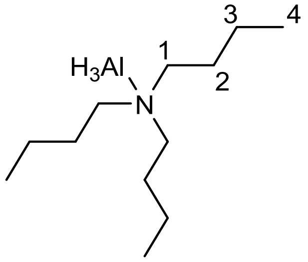
***Scheme S2**: Synthesis procedure for H_3AlNEt_3.*



^{1}H NMR (C_6D_6; 400 MHz): 0.86 (tr; 9H; H2; J = 8 Hz), 2.39 (q; 6H; H1; J = 8 Hz), 4.00 (br s; AlH) ppm. ^{13}C NMR (C_6D_6; 101 MHz): 9.05 (C2), 48.17 (C1) ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 140.84 ppm. δ

IR: Al-H: 1762 cm^{-1}.

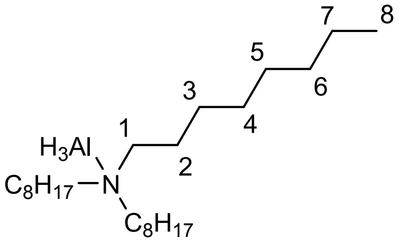
H_3AlNBu_3



^{1}H NMR (C_6D_6; 400 MHz): 0.78 (tr; 9H; H4; J = 8 Hz), 1.06 (sxt; 6H; H3; J = 8 Hz), 1.48-1.56 (m; 6H; H2), 2.46-2.51 (m; 6H; H1), 4.28 (br s; AlH) ppm. ^{13}C NMR (C_6D_6; 101 MHz): 13.90 (C4), 20.97 (C3), 26.42 (C2), 55.23 (C1) ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 163.78 ppm.

IR: Al-H: 1753 cm^{-1}.

$H_3AlN(Oct)_3$



^{1}H NMR (C_6D_6; 400 MHz): 0.91 (tr; 9H; H8; J = 8 Hz), 1.14-1.31 (m; 30H; H7+H6+H5+H4+H3), 1.55-1.61 (m; 6H; H2), 2.53-2.57 (m; 6H; H1), 4.25 (br s; AlH) ppm. Aromatic signals + 2.12 ppm: residual toluene.

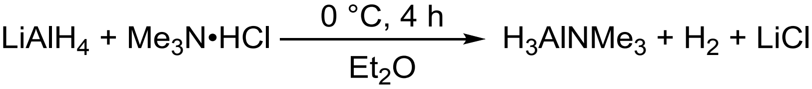
^{13}C NMR (C_6D_6; 101 MHz):14.40 (C8), 23.11, 27.94, 29.74, 29.75, 32.24, 55.36 ppm.

IR: Al-H: 1769 cm^{-1}.

Synthesis of H_3AlNMe_3

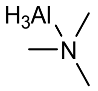
The synthesis was carried out according the methods reported in the literature[4]: 0.5 g (13 mmol) of $LiAlH_4$ and 1.02 g (11 mmol) of $NMe_3 \cdot HCl$ were placed in a 100 ml Schlenk flask and cooled to -50 °C. 50 ml of diethylether were added and the reaction mixture was stirred for 4 h while slowly warming up to room temperature. The solvent was removed in vacuo and 30 ml of hexane were added to the resulting white residue. The reaction mixture was filtered and the filtrate was concentrated in vacuo. After storage at – 25 °C the resulting white solid was collected by filtration and dried in vacuo at 0 °C.

Yield: white solid, 847 mg (72 % based on Al)



$$LiAlH_4 + Me_3N\bullet HCl \xrightarrow[Et_2O]{0\ °C,\ 4\ h} H_3AlNMe_3 + H_2 + LiCl$$

Scheme S3: Synthesis procedure for H_3AlNMe_3.



^{1}H NMR (C_6D_6; 400 MHz): 1.87 (s; 9H), 4.08 (br s; Al-H) ppm.

^{13}C NMR (C_6D_6; 101 MHz): 47.46 ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 140.46 ppm.

IR: Al-H: 1779 cm^{-1}.

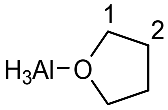
Synthesis of $H_3Al{\cdot}THF$

The preparation was carried out following literature procedures[5]: 1.09 g $LiAlH_4$ (29 mmol) were dissolved in 50 ml THF and the resulting mixture was cooled to 0 °C. 1.26 g $AlCl_3$ (9 mmol) were added in portions and after the complete addition the mixture was stirred for 3 h at 0 °C. The reaction mixture was filtered and the filtrate was concentrated to dryness. 50 ml of hexane were added and the mixture was stirred for 30 min. A white solid was removed by filtration and the filtrate was concentrated in vacuo at room temperature yielding a white solid which was stored under Ar at -10 °C.

Yield: white solid, 3.62 g (92 % based on Al)

$$3\ LiAlH_4 + AlCl_3 \xrightarrow[\text{hexane}]{0\ °C,\ 3\ h} 4\ H_3Al{\bullet}(THF) + 3\ LiCl$$

Scheme S4: Synthesis procedure for $H_3Al{\cdot}THF$.



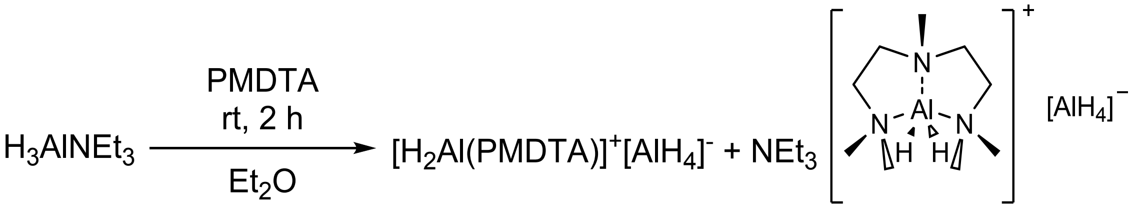
^1H NMR (C_6D_6; 400 MHz): 1.12-1.16 (m; 4H; H2), 3.59-3.63 (m; 4H; H1), 4.21 (br s; AlH) ppm. ^{13}C NMR (C_6D_6; 101 MHz): 25.33 (C2), 69.74 (C1) ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 119.74 ppm.

IR: Al-H: 1807 cm^{-1}.

Synthesis of $[H_2Al(PMDTA)]^+[AlH]^-$

The synthesis was carried out applying known literature methods[6]: Briefly, 1.12 g H_3AlNEt_3 (9 mmol) were dissolved in 25 ml of diethylether. To this solution 1.8 ml (5 mmol) of PMDTA in 15 ml diethylether were added dropwise at 0 °C. The resulting white reaction mixture was stirred for 2 more hours at room temperature before the solvent was evaporated in vacuo. The remaining white solid was recrystallized from THF and stored under Ar at -10 °C.

Yield: white solid, 877 mg (84 % based on Al)



Scheme S5: Synthesis procedure for $[H_2Al(PMDTA)]^+[AlH]^-$.

IR: Al-H: 1662 cm^{-1} + 1826 cm^{-1}

Synthesis of $H_3Al{\cdot}DABCO$

The synthesis was carried out applying known literature methods[7]. 1.02 g DABCO (9 mmol) were dissolved in 30 ml of toluene. To this solution 2.33 g of H_3AlNEt_3 (17 mmol) were added in portions under stirring. The resulting mixture was stirred for 2 h at room temperature. The solvent was evaporated in vacuo and the resulting white solid was washed with diethylether and stored under Ar at –10 °C.

Yield: white solid, 2.49 g (97%). The product was obtained as a mixture of H_3AlNEt_3 and $H_3Al{\cdot}DABCO$

$$H_3AlNEt_3 \xrightarrow[Et_2O]{\text{DABCO, rt, 2 h}} H_3Al{\bullet}(DABCO) + NEt_3$$

Scheme S6: Synthesis procedure for $H_3Al{\cdot}DABCO$.

IR: Al-H: 1691 cm^{-1} + 1762 cm^{-1}

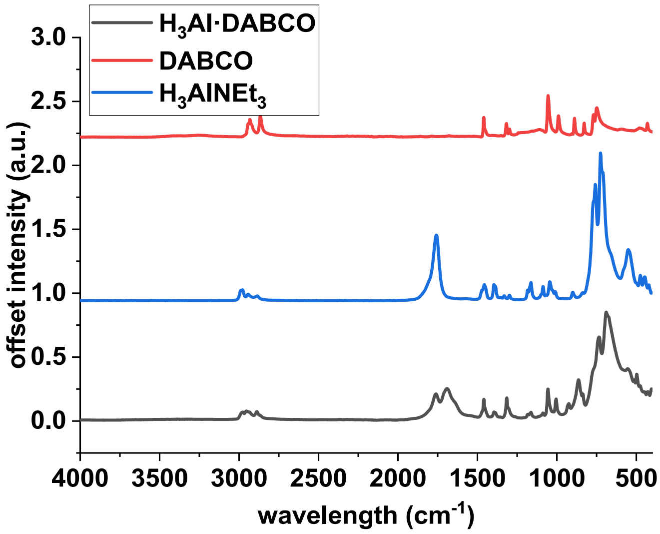
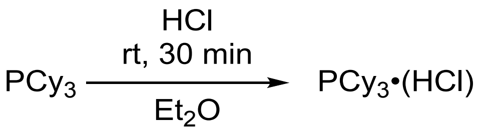


Figure S29: ATR-FTIR spectra of $H_3Al{\cdot}DABCO$, H_3AlNEt_3 and DABCO.

Synthesis of $H_3Al{\cdot}PCy_3$

Protocols reported in the literature were applied[8]: Briefly, a solution of 1.5 g of PCy_3 (5 mmol) in 10 ml of diethylether was bubbled with HCl under stirring for 30 min. A white solid was formed and the solvent was removed in vacuo.

Yield: 1.63 g (97 %)



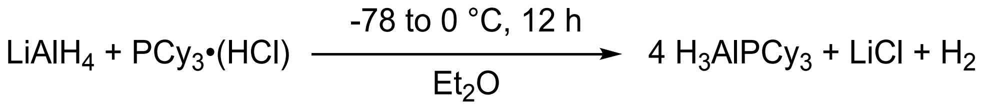
$$PCy_3 \xrightarrow[Et_2O]{\text{HCl, rt, 30 min}} PCy_3{\bullet}(HCl)$$

Scheme S7: Synthesis procedure for $PCy_3{\cdot}HCl$.

^1H NMR ($CDCl_3$; 400 MHz): 1.29-2.57 (m; 33H; Cy), 7.81 (d; 1H; P-H; J = 492 Hz). ^{31}P NMR ($CDCl_3$; 162 MHz): 31.35 (d; J = 491 Hz) ppm.

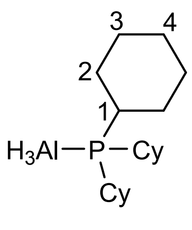
To a mixture of 302 mg $LiAlH_4$ (8 mmol) and 1.6 g $PCy_3{\cdot}HCl$ (5 mmol) was added 70 ml of diethylether at -78 °C. The mixture was stirred over night while warming up to room temperature. The formed solid was filtered off and the filtrate was concentrated to dryness. The resulting white solid was recrystallized from diethylether and stored under Ar at -10 °C.

Yield: white solid, 490 mg (32 % based on Al)



$$LiAlH_4 + PCy_3{\bullet}(HCl) \xrightarrow[Et_2O]{-78\text{ to }0\ ^\circ C,\ 12\text{ h}} 4\ H_3AlPCy_3 + LiCl + H_2$$

Scheme S8: Synthesis procedure for $H_3Al{\cdot}PCy_3$.

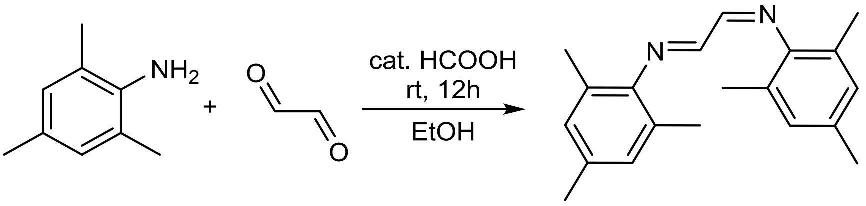


^{1}H NMR (C_6D_6; 400 MHz): 0.98-1.08 (m; 9H; Cy), 1.42-1.59 (m; 15H; Cy), 1.81-1.87 (m; 9H; Cy), 4.26 (br s; AlH) ppm. ^{31}P NMR (C_6D_6; 162 MHz): 3.57 ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 118.67 ppm. IR: Al-H: 1750 cm^{-1}

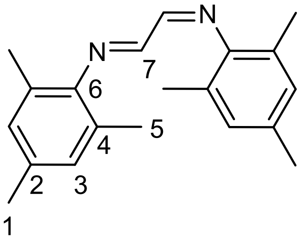
Synthesis of $H_3Al\cdot IMes$

The synthesis was carried out applying known literature methods[9,10]. Under an atmosphere of air, 58 ml (0.5 mol) glyoxal (40 % w/w in H_2O) were added to 54 g (0.4 mol) of 2,4,6-trimethylaniline in 200 ml of methanol. 0.5 ml of formic acid were added dropwise and the reaction mixture was stirred over night at room temperature. The formed yellow solid was collected, washed with 50 ml of methanol and dried in vacuo.

Yield: yellow solid, 54 g (92 %)



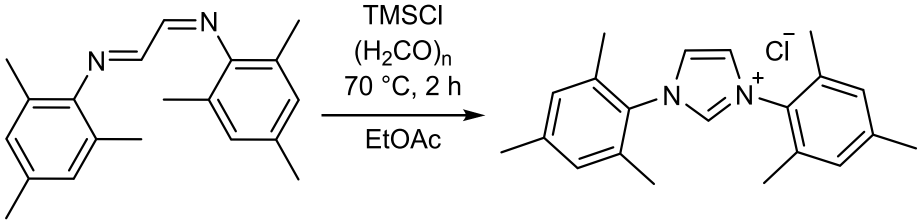
Scheme S9: Synthesis procedure for N[1],N[2]-dimesitylethane-1,2-diimine.



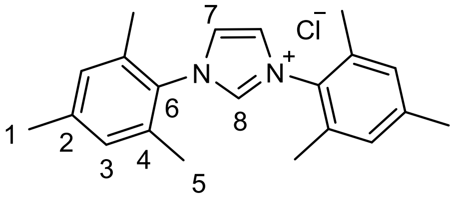
^{1}H NMR ($CDCl_3$; 400 MHz): 2.16 (s; 12H; H5), 2.30 (s; 6H; H1), 6.91 (s; 4H; H3), 8.11 (s; 2H; H7) ppm. ^{13}C NMR ($CDCl_3$; 101MHz): 18.34 (C5), 20.91 (C1), 126.70 (C4), 129.13 (C3), 134.40 (C2), 147.60 (C6), 163.63 (C7) ppm.

Under an atmosphere of air, 5 g of (17 mmol) N^1,N^2-dimesitylethane-1,2-diimine were dissolved in 120 ml of ethylacetate and 0.55 g (18 mmol) paraformaldehyde were added. 2.5 ml (20 mmol) TMSCl dissolved in 15 ml of ethylacetate were added dropwise and the reaction mixture was heated to 70 °C for 2 h. The formed solid was collected by filtration, washed with ethylacetate and dried at 100 °C.

Yield: very slight yellow solid, 2.6 g (45 %)



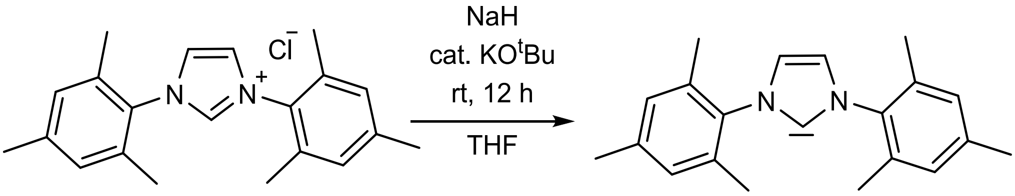
Scheme S10: Synthesis procedure for 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride.



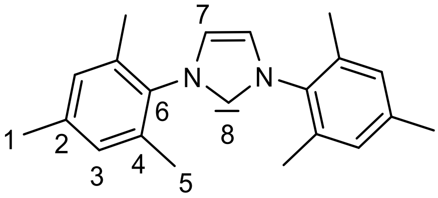
^{1}H NMR ($CDCl_3$; 400 MHz): 2.19 (s; 12H; H5), 2.34 (s; 6H; H1), 7.03 (s; 4H; H3), 6.91 (s; 4H; H3), 7.58 (s; 2H; H7), 11.03 (s; 1H; H8) ppm. ^{13}C NMR ($CDCl_3$; 101MHz): 17.82 (C5), 21.28 (C1), 124.37 (C6), 130.09 (C3), 130.77 (C2), 134.22 (C4), 141.49 (C7) ppm.

1 g (3 mmol) of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride were dispersed in 40 ml of THF. 150 mg (6 mmol) NaH and a grain of KO^{t}Bu were added and the resulting mixture was stirred over night at room temperature. The remaining solid was filtered off and the filtrate was concentrated in vacuo. The product was precipitated by adding 40 ml of Hexane, collected by filtration and dried in vacuo.

Yield: white solid, 687 mg (75 %)



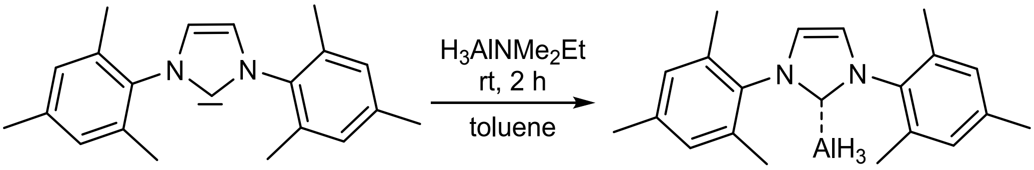
Scheme 11: Synthesis procedure for 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene (IMes).



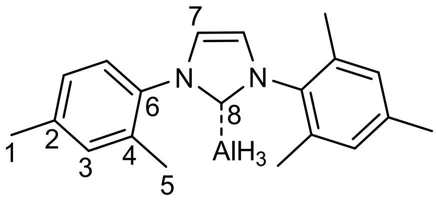
^{1}H NMR (C_6D_6; 400 MHz): 2.16 (s; 18H; H1+H5), 6.49 (s; 2H; H7), 6.81 (s; 4H; H3) ppm.
^{13}C NMR (C_6D_6; 101MHz): 18.07 (C5), 21.04 (C1), 120.56 (C7), 135.46 (C6), 137.28 (C4), 139.28 (C3), 219.18 (C8) ppm.

To a solution of 201 mg (0.7 mmol) of 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene in 20 ml of toluene were added 1.3 ml (0.7 mmol) of a 0.5 M solution of H_3AlNMe_2Et in toluene. The mixture was stirred for 2 h at room temperature and then dried in vacuo yielding a white to light yellow solid.

Yield: white solid, 154 mg (66%)



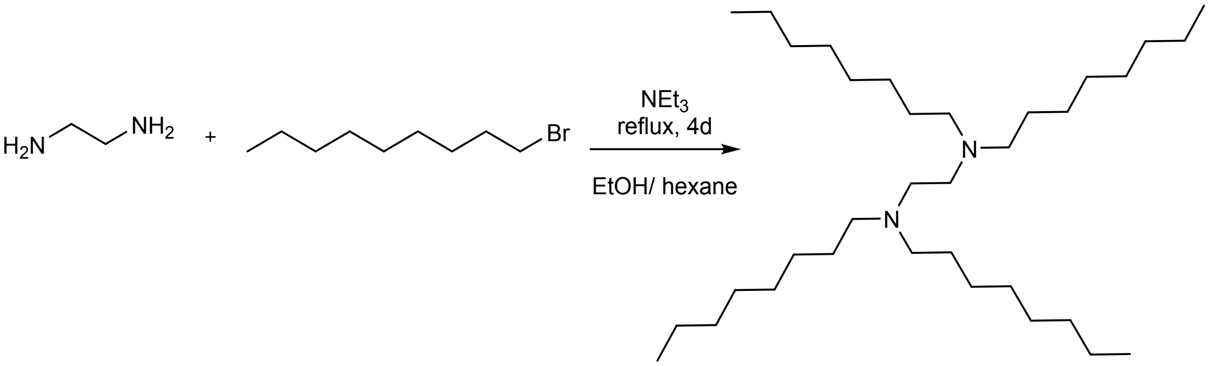
Scheme S12: Synthesis procedure for $H_3Al{\cdot}IMes$.



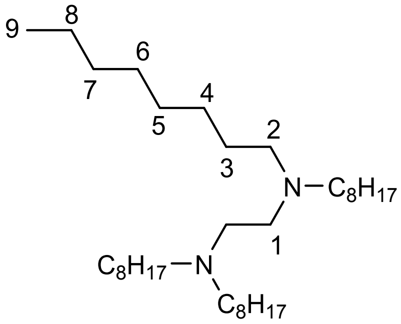
^{1}H NMR (C_6D_6; 400 MHz): 2.04 (s; 12H; H5), 2.07 (s; 6H; H1), 6.49 (s; 2H; H7), 3.79 (br s; AlH), 6.04 (s; 2H; H7), 6.74 (s; 4H; H3) ppm. ^{13}C NMR (C_6D_6; 101MHz): 17.63 (C5), 21.09 (C1), 122.50 (C7), 129.48 (C4), 130.02 (C2), 135.04 (C3), 139.55 (C6) ppm. ^{27}Al NMR (C_6D_6; 104 MHz): 117.54 ppm. IR: Al-H: 1741 cm^{-1}.

Synthesis of N,N,N′,N′-tetraoctylethylendiamine (TOEDA)

The synthesis was carried out applying known literature methods[11]. In an atmosphere of air, 1,45 ml (22 mmol) of ethylendiamine were dissolved in 5 ml of methanole/ hexane (50/50 v/v) and 15 ml of triethylamine were added. 15 ml (87 mmol) of 1-bromoctane were added dropwise and the reaction mixture was heated to reflux for 4 days. The formed solid was filtered off and the filtrate was concentrated to dryness. The viscous residue was dissolved in toluene, and the pH was adjusted to 7 using HCl/ NaOH. The organic phase was washed three times with 50 ml of H_2O, dried with $MgSO_4$ and the solvent was removed in vacuo.



Scheme S13: Synthesis procedure for N,N,N′,N′-tetraoctylethylendiamine (TOEDA).



^{1}H NMR ($CDCl_3$; 400 MHz): 0.86 (tr; 12H; H9; J = 8 Hz), 1.25-1.40(m; 48H; H2+H3+H4+H5+H6+H7), 2.38 (tr; 8H; H2), 2.48 (s; 4H; H1) ppm. ^{13}C NMR ($CDCl_3$; 101MHz): 14.14 (C9), 22.74, 27.27, 27.69, 29.41, 29.69, 31.96, 52.41(C1), 54.95 (C2) ppm.

From the selected precursors the hydrogen content was determined by NMR spectroscopy and from a titriometric method (**Table S2**)[1] [2], in order the determine the excatct amount of Al introduced into the reaction mixtures. The titriometric method was used in addition to the NMR integration for the determination of the hydride content, since the hydridic protons are typically resulting in broad ^{1}H NMR signals making their integration difficult. However, in our studies a good agreement between the two methods could be achieved. The observed hydride content typically is slightly below the expected value of three, most likely based on the formation of a few 2:1 complexes.

Table S2: Overview of the Al precursors applied for the synthesis of Al nanoparticles.

Donor atom	**Precursor**	**M_w [g/mol]**	**H/Al^1**	**H/Al^2**
N	H_3AlNMe_3	89.12	2.54	2.66
	H_3AlNEt_3	131,19	2,64	2,73
	$H_3AlNEtMe_2$	101,14	2,76	---
	$H_3AlN^nBu_3$	215,35	2,39	2,35
	$H_3AlN^nOct_3$	383,67	2,60	2,18
polymeric	$H_3Al{\cdot}DABCO$	142,17	2,27	---
ionic	$H_3Al{\cdot}PMDTA$	233,30	2,23	---
O	$H_3Al{\cdot}THF$	110,11	1,72	2,28
P	$H_3Al{\cdot}PCy_3$	310,43	2,87	2,60
C	$H_3Al{\cdot}IMes$	334,43	2,44	2,35

^{1}titriometric method, ^{2}NMR integration

References

(1) Fedotova, T. D.; Glotov, O. G.; Zarko, V. E. Chemical Analysis of Aluminum as a Propellant Ingredient and Determination of Aluminum and Aluminum Nitride in Condensed Combustion Products. *Propellants, Explos. Pyrotech.* **2000**, *25*, 325–332.

(2) Yang, S.-P.; Tsai, R.-Y. Complexometric Titration of Aluminum and Magnesium Ions in Commercial Antacids. An Experiment for General and Analytical Chemistry Laboratories. *J. Chem. Educ.* **2006**, *83*, 906.

(3) Reuvers, P. J.; Smit, C. J. Preparation and Properties of Alane Dimethylethylamine, a Liquid Precursor for MOCVD. *Chem. Mater.* **1994**, *6*, 190–195.

(4) Ruff, J. K.; Hawthorne, M. F. The Amine Complexes of Aluminum Hydride. I. *J. Am. Chem. Soc.* **1960**, *82*, 2141–2144.

(5) Finholt, A. E.; Bond, A. C.; Schlesinger, H. I. Lithium Aluminum Hydride, Aluminum Hydride and Lithium Gallium Hydride, and Some of Their Applications in Organic and Inorganic Chemistry 1. *J. Am. Chem. Soc.* **1947**, *69*, 1199–1203.

(6) Atwood, J. L.; Robinson, K. D.; Jonesb, C.; Raston, C. L. Cationic Aluminium Hydrides: $[H_2AlL]+[AlH_4]-$, L = N,N,N',N",N"-Pentamethyldiethylenetriamine and 1,4,8,11-Tetramethyl-1,4,8,11-Tetraazacyclotetradecane. *J. Chem. Soc., Chem. Commun.* **1991**, *3*, 1697–1699.

(7) Brown, H. C.; Singaram, B. Molecular Addition Compounds. 7. Synthesis of Addition Compounds of Boron Trifluoride, Borane, and Alane with N, N, N, 'N'-Tetramethylethylenediamine and Triethylenediamine by Precipitation from Ether Solvents. *Inorg. Chem.* **1980**, *19*, 455–457.

(8) Bennett, F. R.; Elms, F. M.; Gardiner, M. G.; Koutsantonis, G. A.; Raston, C. L.; Roberts, N. K. Stable Tertiary Phosphine Adducts of Alane. *Organometallics* **1992**, *11*, 1457–1459.

(9) Bantreil, X.; Nolan, S. P. Synthesis of N-Heterocyclic Carbene Ligands and Derived Ruthenium Olefin Metathesis Catalysts. *Nat. Protoc.* **2011**, *6*, 69–77.

(10) Hintermann, L. Expedient Syntheses of the N-Heterocyclic Carbene Precursor Imidazolium Salts IPr·HCl, IMes·HCl and IXy·HCl. *Beilstein J. Org. Chem.* **2007**, *3*, 2–6.

(11) Preez, J. G. H. du; Shillington, D. P.; Brecht, B. J. A. M. van. Polynitrogen Reagents in Metal Separation. Part 1. Ditertiary and Diquaternary Ammonium Extractants for Cobalt (II) and Copper (II) in HCL Medium. *Solvent Extr. Ion Exch.* **2007**, *2*, 839–858.