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SUPPORTING INFORMATION

Title: Organometallic Access to Intermetallic θ-CuE_2 (E = Al, Ga) and $Cu_{1-x}Al_x$ Phases
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1. Syntheses

a) Synthesis of $Cu_{1-x}Al_x$ powder from [CpCu(PMe$_3$)] and [(AlCp*)$_4$]

In a Fischer-Porter bottle, [CpCu(PMe$_3$)] (0.100 g, 0.488 mmol) and [(AlCp*)$_4$] (masses see Table S1) were combined in 10 mL mesitylene, treated with 3 bar H_2 and set into a 150 °C hot oil bath. After few minutes, the yellow solution became darker and after 15 min, a grey precipitate formed. After 3 h of stirring at 150 °C, the precipitated grey $Cu_{1-x}Al_x$ powder was isolated as described above. Since the product contained impurities (according to XRD), the powder was washed with 3 x 50 mL 1,4-dioxane and 3 x 50 mL *n*-pentane.

Data for x = 0.67: EDX analysis: Al, 69 %; Cu, 31 %. ^{27}Al MAS NMR (104.2 MHz, 25 °C, ν = 10 KHz): δ 1486 (Knight shift of Al^0 in $CuAl_2$), 56.1 and 1.9 (Al_2O_3). XRD data are listed in Table S2.

Table S1. Required masses of [(AlCp*)$_4$] for the synthesis of the $Cu_{1-x}Al_x$ phases.

$Cu_{1-x}Al_x$	m([(AlCp*)$_4$])	Elemental analysis (after washing)	Yield (after washing)
x = 0.67	0.159 g (0.245 mmol)	Cu, 45.1; Al, 41.7	0.047 g (82 %)
x = 0.50	0.079 g (0.122 mmol)	Cu, 54.1; Al, 27.2	0.038 g (86 %)
x = 0.31	0.035 g (0.054 mmol)	Cu, 72.6; Al, 14.4	0.029 g (79 %)

Table S2. Comparison of XRD reflections (2θ/°) of synthesized θ-CuAl$_2$ and reference data (JCPDS No. 25-0012).

h k l (Int. in %)	CuAl$_2$ from [CpCu(PMe$_3$)] and [(AlCp*)$_4$]	CuAl$_2$ from [CpCu(PMe$_3$)] and [(Me$_3$N)AlH$_3$]	CuAl$_2$ from [{Cu(mesityl)}$_5$] and [(Me$_3$N)AlH$_3$]	CuAl$_2$ reference
1 1 0 (100)	20.68	20.74	20.70	20.620
2 0 0 (35)	29.47	29.54	29.45	29.386
2 1 1 (70)	38.01	38.03	37.98	37.867
2 2 0 (35)	42.20	42.24	42.21	42.071
1 1 2 (90)	42.68	42.73	42.69	42.591
3 1 0 (70)	47.44	47.51	47.45	47.332
2 0 2 (60)	47.91	47.95	47.85	47.808
2 2 2 (13)	57.26	57.32	57.27	57.129
4 0 0 (2)	61.65	61.63	61.58	61.032
3 1 2 (6)				61.435
4 1 1 (6)	66.40	66.51	66.46	66.335
2 1 3 (9)	67.21	67.28	67.21	67.034
4 2 0 (11)	69.33	69.42	69.38	69.173
4 0 2 (21)	73.62	73.73	73.64	73.462
3 3 2 (20)	77.48	77.59	77.49	77.251
0 0 4 (8)	78.41	78.51	78.37	78.382
5 1 0 (11)	81.16	81.38	81.15	80.678
4 2 2 (11)				81.007
4 3 1 (9)	82.44	82.43	82.42	81.842
1 1 4 (9)				82.181
2 0 4 (1)	86.12	86.04	86.04	85.950
5 2 1 (5)	89.43	89.50	89.41	89.103
4 1 3 (3)	90.10	90.03	90.04	89.829
4 4 0 (3)	92.06	92.21	92.37	91.872
5 1 2 (5)	93.28	92.51		92.205
3 2 4 (3)	93.50	93.64	93.47	93.220
5 3 0 (2)	95.78	95.91	95.82	95.577
3 1 4 (17)	97.18	97.29	97.19	97.063
6 0 0 (5)	99.54	99.66	99.50	99.267

2. Additional figures

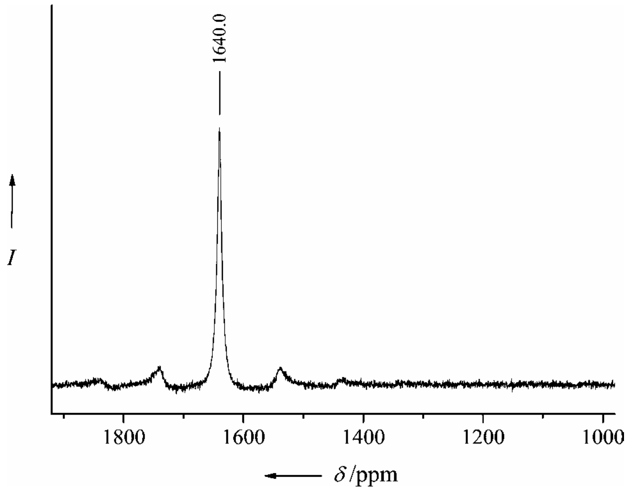

Figure S1. ^{27}Al MAS NMR of Al particles, obtained by decomposition of [(Me$_3$N)AlH$_3$] (sample diluted with SiO$_2$).

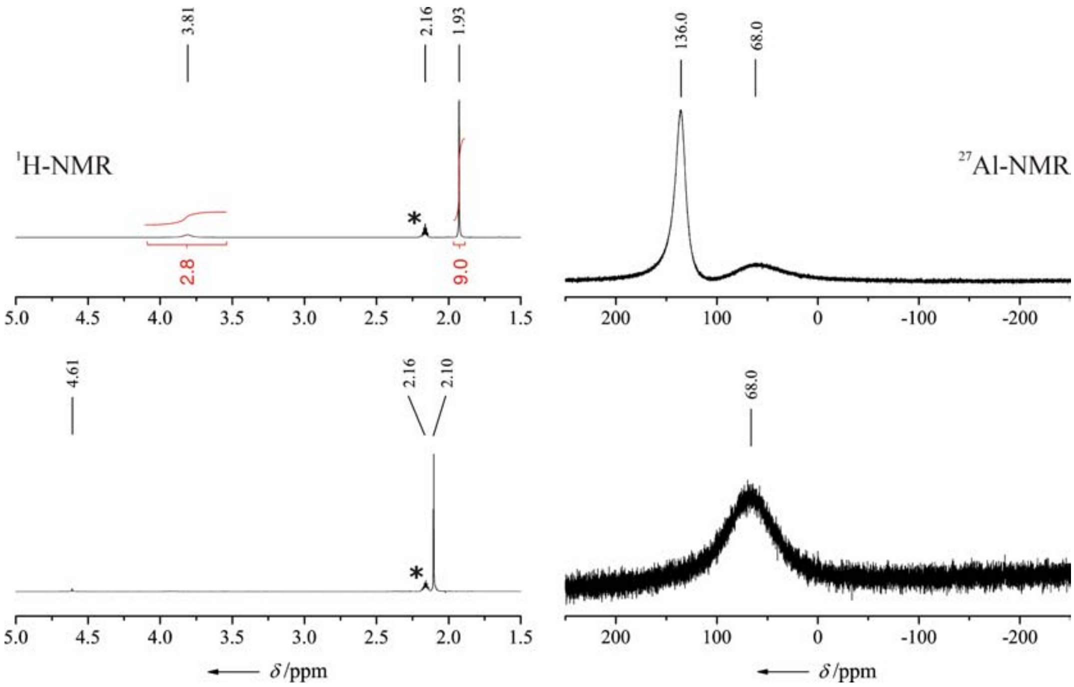

Figure S2. ^{1}H- and ^{27}Al NMR spectra of [(Me$_3$N)AlH$_3$] in d$_{12}$-mesitylene before decomposition (upper spectra) and after decomposition in a pressure stable NMR tube with 3 bar H$_2$ at 150 °C (lower spectra). The large broad signal at around 68 ppm represents the static signal of the probe head of the spectrometer. The asterisks mark the residual proton signals of the methyl groups of d$_{12}$-mesitylene.

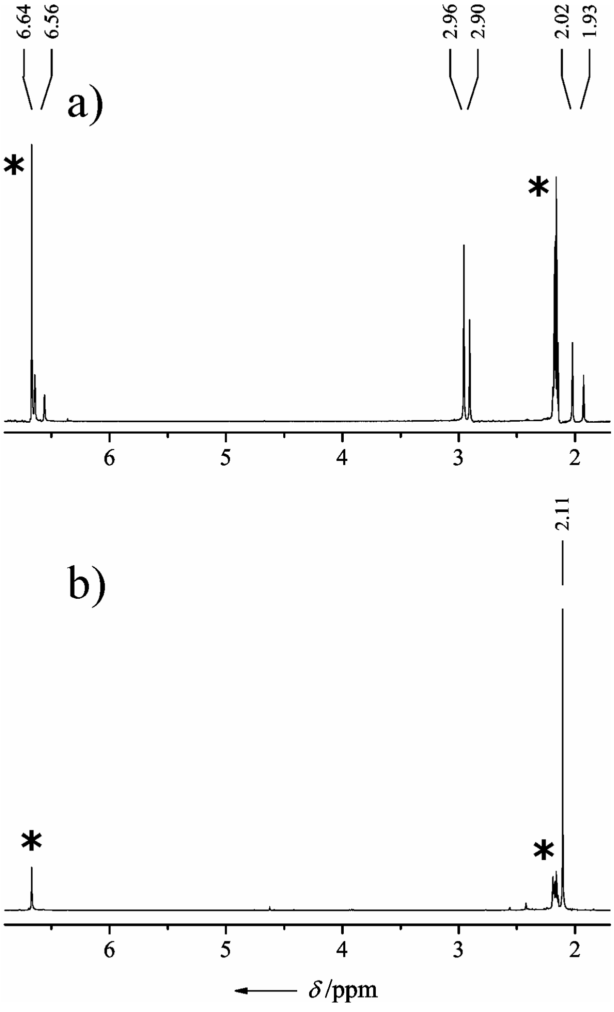

Figure S3. Left: ^{1}H NMR spectra (in d$_{12}$-mesitylene) of a) [{Cu(mesityl)}$_5$], b) after co-hydrogenolysis of [{Cu(mesityl)}$_5$] and 10 equiv. [(Me$_3$N)AlH$_3$] for 24 h at 4 bar H$_2$/150 °C. The asterisks represent the solvent signals (ring H: 6.67 ppm, methyl H: 2.16 ppm).

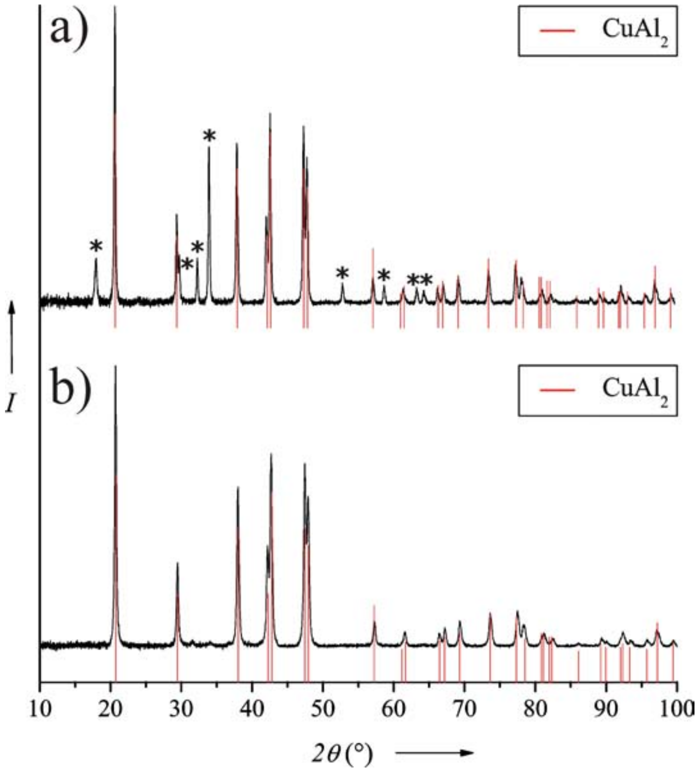

Figure S4. XRD diagrams of the θ-CuAl$_2$ phase, a) obtained by co-hydrogenolysis of [CpCu(PMe$_3$)] and 0.5 equiv. [(AlCp*)$_4$] before purification, b) after washing the powder of (a) with 1,4-dioxane.

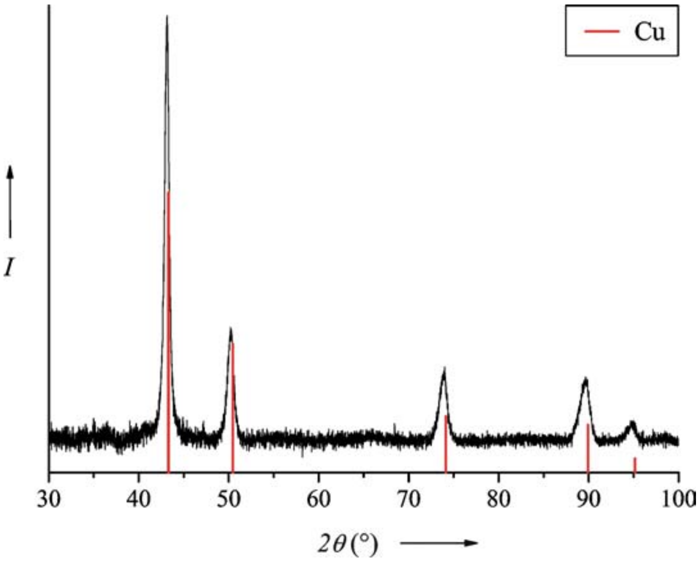

Figure S5. XRD pattern of the powder obtained by co-hydrogenolysis of 9 equiv. of [CpCu(PMe$_3$)] and 1 equiv. of [(AlCp*)$_4$] at reaction conditions of 3 bar H$_2$ pressure and 150 °C in mesitylene.

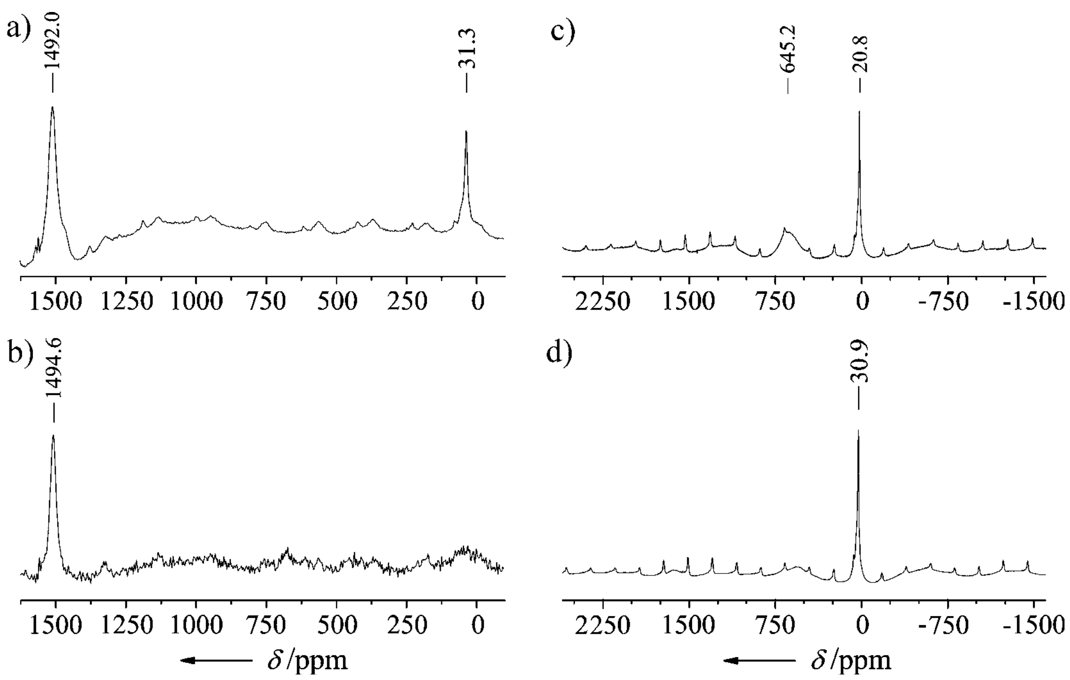

Figure S6. ^{27}Al MAS NMR spectra of the samples of a) θ-$CuAl_2$ obtained from [CpCu(PMe_3)] with 2 equiv. [(Me_3N)AlH_3], b) θ-$CuAl_2$ obtained from [{Cu(mesityl)}$_5$] with 10 equiv. [(Me_3N)AlH_3], c) $Cu_{0.51}Al_{0.49}$ synthesized from [{Cu(mesityl)}$_5$] with 5 equiv. [(Me_3N)AlH_3] and d) γ-Cu_9Al_4 synthesized from [{Cu(mesityl)}$_5$] with 2.2 equiv. [(Me_3N)AlH_3].