Electronic Supplementary Material (ESI) for Chemical Communications.


# Supporting Information

## A Combinatorial Coordination Modulated Approach to All-Hydrocarbon Ligated Intermetallic Clusters

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**Experimental and Analytical Data**

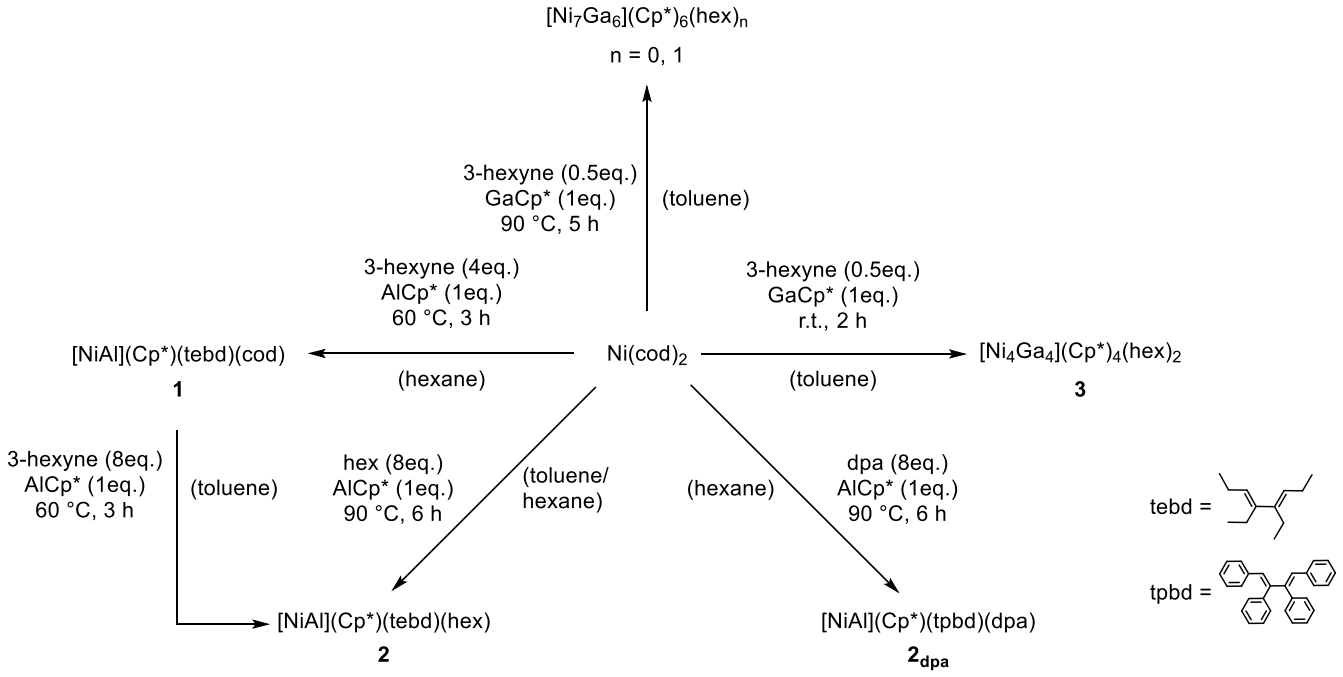
## General remarks

All manipulations were carried out using standard Schlenk techniques under inert atmospheres. Solvents were dried using a MBraun Solvent Purification System. The final $H_2O$ content of all solvents was checked by Karl Fischer titration and was below 5 ppm. Starting materials $[Ni(cod)_2]$[1], GaCp*[2], and AlCp*[3] were synthesized according to literature procedures. Elemental analysis was performed at the microanalytical laboratory at the Technical University Munich. NMR spectra were recorded on a Bruker AV 400 US spectrometer, a Bruker DRX 400 ($^1$H, 400 MHz; $^{13}$C, 101 MHz) or a Bruker AV500 ($^1$H, 500 MHz; $^{13}$C, 126 MHz) usually in $C_6D_6$, toluene-$d_8$ or cyclohexane-$d_{12}$. Chemical shifts (in δ) are described in ppm relative to tetramethylsilane (TMS) and referenced to the solvent resonances as internal standards. Liquid injection field desorption ionization mass spectrometry (LIFDI-MS) data were measured on an Exactive Plus Orbitrap system by Thermo Fisher Scientific equipped with an ion source (LIFDI) from LINDEN CMS GmbH. The samples were dissolved in either dry toluene or hexane and filtered over a syringe filter under an inert atmosphere. Infrared spectra were measured on an Alpha FT-IR from Bruker equipped with an ATR device using a platinum diamond in a glovebox LABstarPro ECO from M.Braun. The interferometer measured in a range of 400 to 4000 $cm^{-1}$. The compounds were measured under inert atmosphere in a glovebox. UV-vis spectra were recorded on a double beam Lambda 365 UV–Vis spectrophotometer from PerkinElmer.

## Computational details

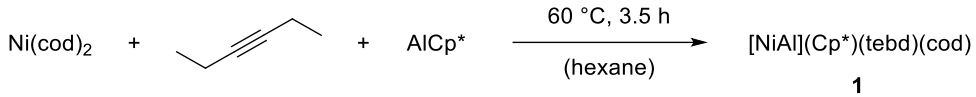
Geometries of the related molecules were optimized using the ORCA4.0[4] software package and Becke's exchange functional[5] with Perdew's correlation functional[6] (BP86). Grimme's Dispersion correction including Becke-Johnson damping (D3BJ)[7] was used. After preoptimization and analytical calculation of the Hessian using Ahlrich's def2-SVP basis set these structures were further optimized using the def2-TZVPP basis sets.[8] The resolution of identity approximation (RI) was applied to speed up the calculations.[9] Time-dependent density functional theory (TDDFT) calculations were performed to compute the UV-Vis spectra and included the lowest 50 eigenvalues.

## Overview of the reactions



## [NiAl](Cp*)(tebd)(cod) (**1**)

### Synthesis procedure




$Ni(cod)_2$ (100 mg, 0.364 mmol, 1.0 eq.) was suspended in 1 mL hexane and 3-hexyne (1.41 mL, 1.41 mmol, 3.9 eq) was added as a 1 M solution in hexane to give a red solution within seconds. Afterwards, AlCp* (60 mg, 0.370 mmol, 1.0 eq.) was added and the reaction mixture was stirred at 60 °C for 3.5 h giving a greenish-brown solution. After slowly cooling to -30 °C overnight, yellow crystals could be obtained which were dried in *vacuo* after filtration (yield: 15 %).

**$^1$H NMR** (400 MHz, 293 K, toluene-$d_8$): δ (ppm) = 4.43 – 4.33 (m, 2H, C=C*H*), 3.40 (dt, $^3J$ = 5.0 Hz, 2H, C=C*H*), 2.45 – 2.32 (m, 2H, CHC$H_2$), 2.25 – 2.12 (m, 4H, CHC$H_2$), 2.12 – 2.08 (m, 2H, C$H_2$CH$_3$), 2.08 – 1.99 (m, 4H, C$H_2$CH$_3$), 1.97 (s, 15H, C$_5$(C$H_3$)$_5$), 1.96 – 1.89 (m, 2H, CHC$H_2$), 1.77 (dq, $^3J$ = 14.4, $^3J$ = 7.4 Hz, 2H (m, 2H, C$H_2$CH$_3$), 1.25 (t, $^3J$ = 7.5 Hz, 6H, CH$_2$C$H_3$), 1.17 (t, $^3J$ = 7.5 Hz, 6H, CH$_2$C$H_3$). *Note: The signal intensity of the multiplet at 2.25 - 2.10 ppm is higher than expected due to the overlap with the methyl group of the solvent (toluene).*

**$^{13}$C NMR** (101 MHz, 293 K, toluene-$d_8$): δ (ppm) = 129.5 (Al-$C_4$), 114.5 ($C_5$Me$_5$), 88.7 (*C*HCH$_2$), 79.6 (*C*HCH$_2$), 32.2 (CH*C*H$_2$), 31.3 (CH*C*H$_2$), 26.4 (*C*H$_2$CH$_3$), 20.4 (*C*H$_2$CH$_3$), 18.1 (CH$_2$*C*H$_3$), 16.8 (CH$_2$*C*H$_3$), 11.8 (C$_5$*Me*$_5$).

**IR (ATR, neat, cm$^{-1}$):** 2958, 2905, 2865, 2921, 2725, 1738, 1669, 1600, 1511, 1448, 1431, 1376, 1326, 1298, 1260, 1240, 1152, 1097, 1063, 1022, 855, 799, 727, 589.

**HRMS (LIFDI, toluene):** m/z calcd for $C_{30}H_{47}NiAl$: 492.2847; found: 492.2822.

**UV/Vis** (*n*-hexane): $\lambda_{max}$ = 285, 220 nm.

### NMR spectroscopic data of 1

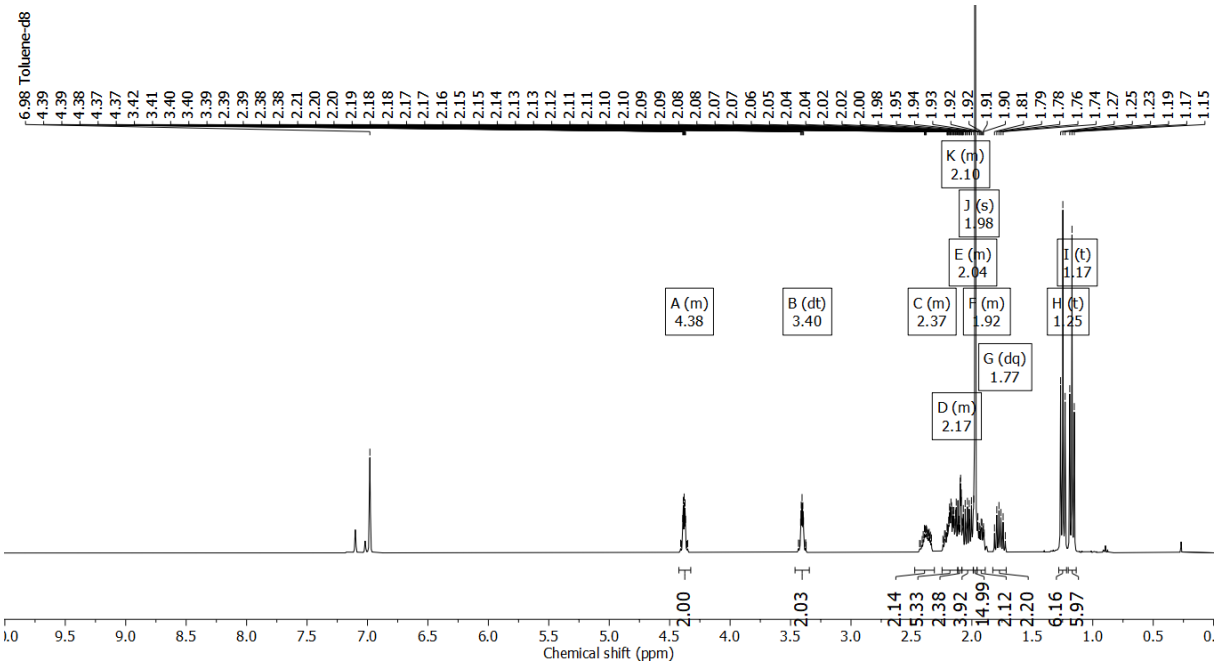



Fig. S 1. $^1$H NMR spectrum of [NiAl](Cp*)(tebd)(cod) (**1**) in toluene-$d_8$. Note: The signal intensity of the multiplet at 2.25 - 2.10 ppm is higher than expected due to the overlap of the signal for the methyl group of the solvent (toluene).

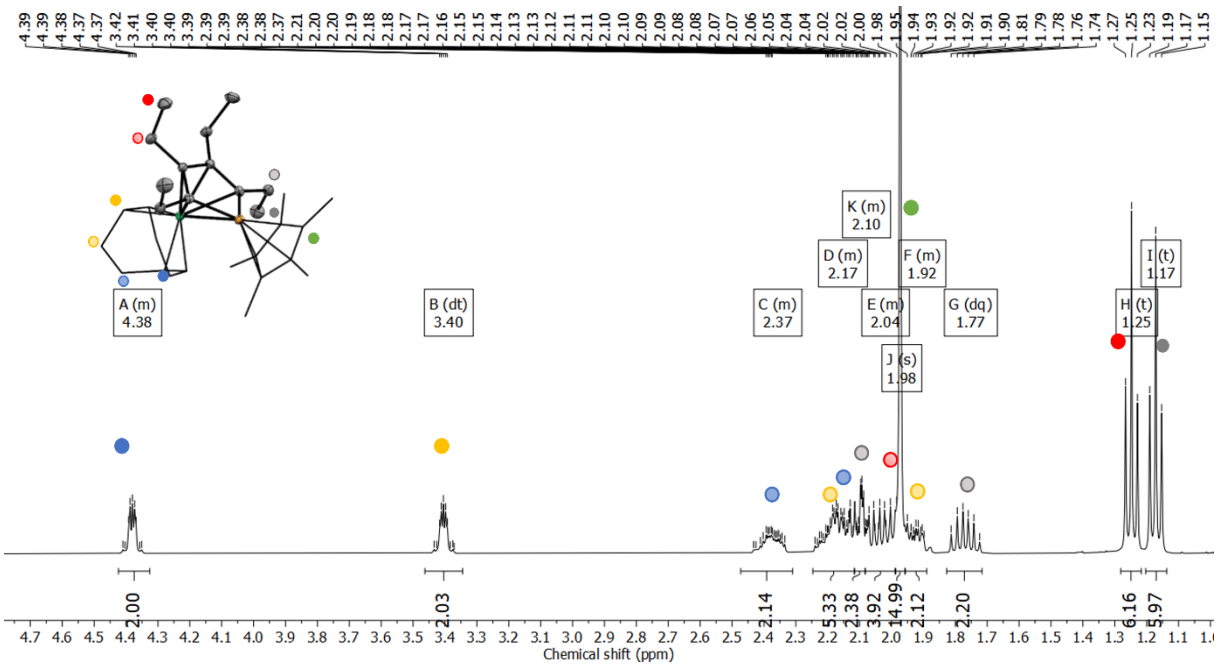



Fig. S 2. $^{1}$H NMR spectrum of **1** in toluene-$d_8$ with signal assignment.

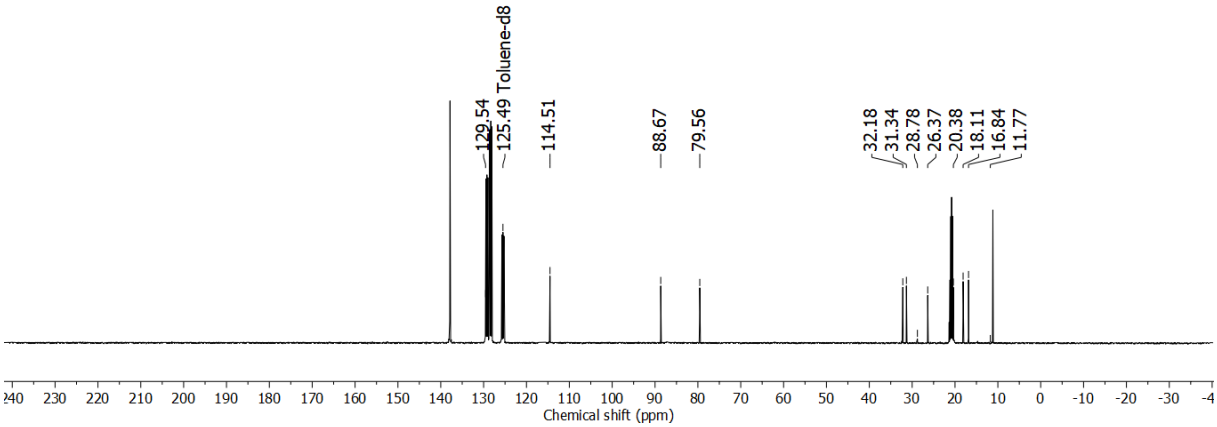



Fig. S 3. $^{13}$C NMR spectrum of [NiAl](Cp*)(cod)$_1$(hex)$_2$ (**1**) in toluene-$d_8$.

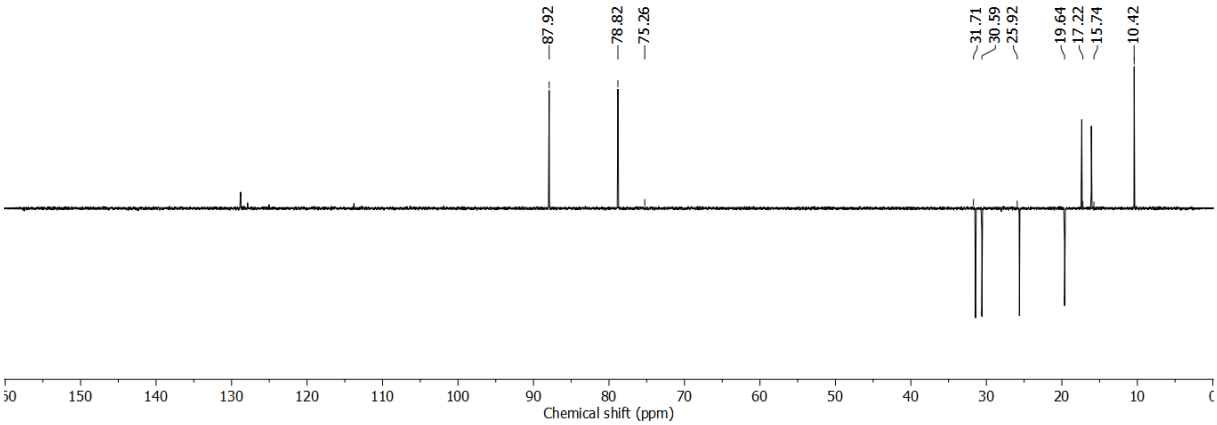



Fig. S 4. DEPT 135 NMR spectrum of **1** in toluene-$d_8$. Negative signals refer to $CH_2$ groups, whereas positive signals are assigned as CH or $CH_3$ groups.

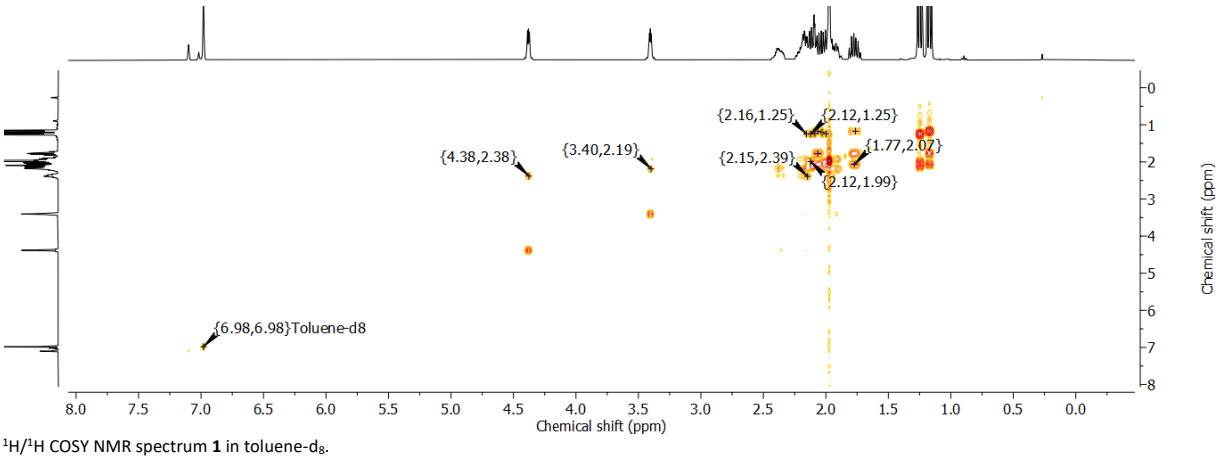



Fig. S 5. $^{1}H/^{1}H$ COSY NMR spectrum **1** in toluene-$d_8$.

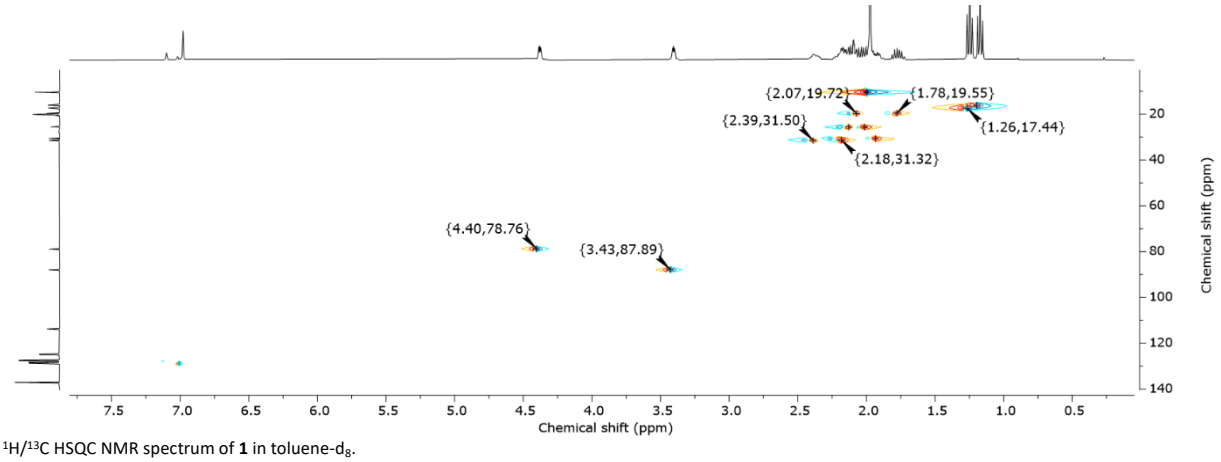



Fig. S 6. $^{1}H/^{13}C$ HSQC NMR spectrum of **1** in toluene-$d_8$.

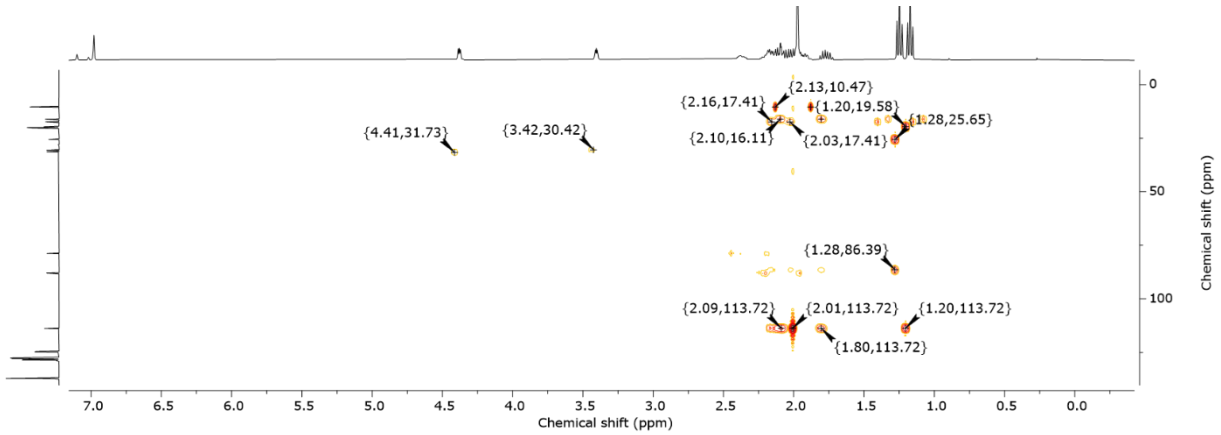



Fig. S 7. $^{1}H/^{13}C$ HMBC NMR spectrum of **1** in toluene-$d_8$.

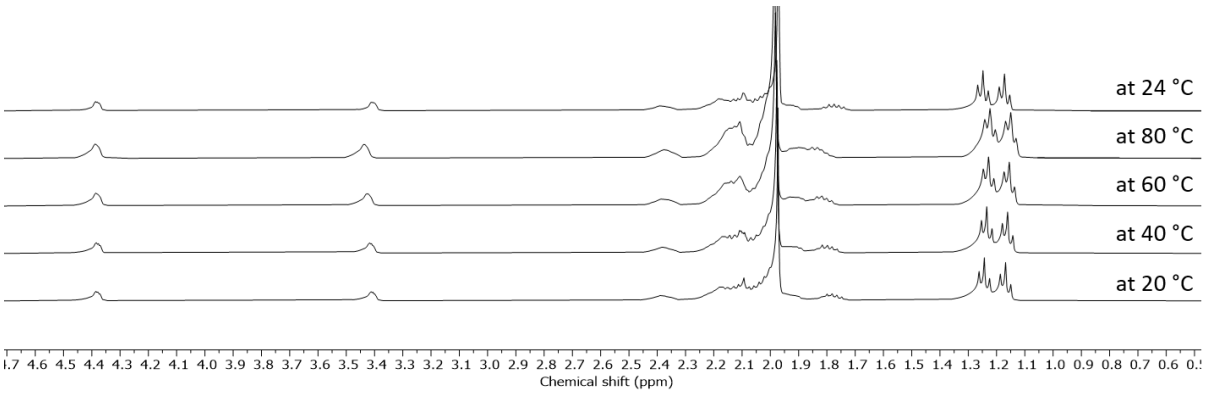



Fig. S 8. High temperature $^{1}H$ NMR studies of **1** in toluene-$d_8$.

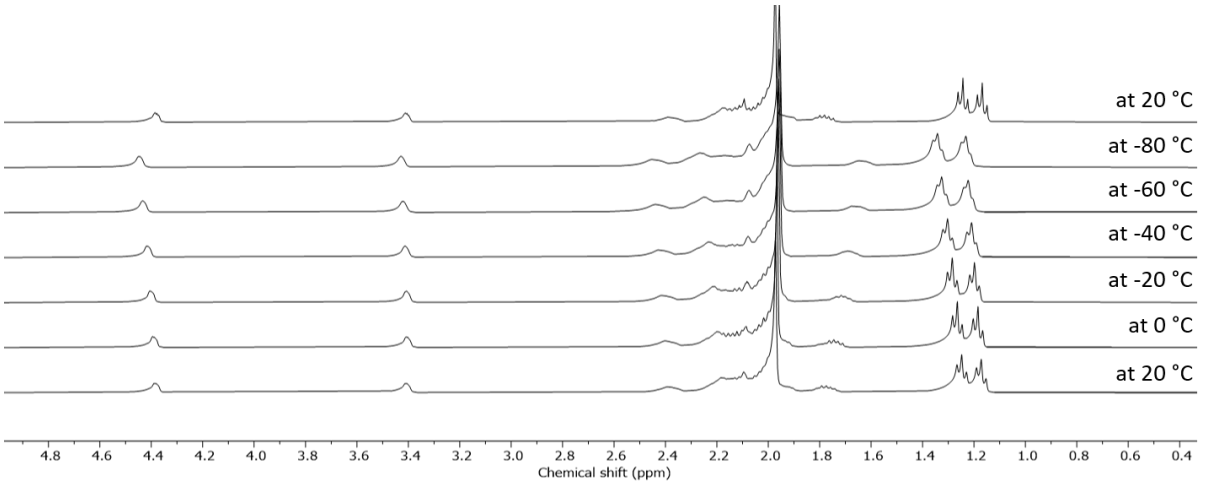



Fig. S 9. Low temperature $^{1}H$ NMR studies of **f** in toluene-$d_8$.

## Mass spectrometric data of 1

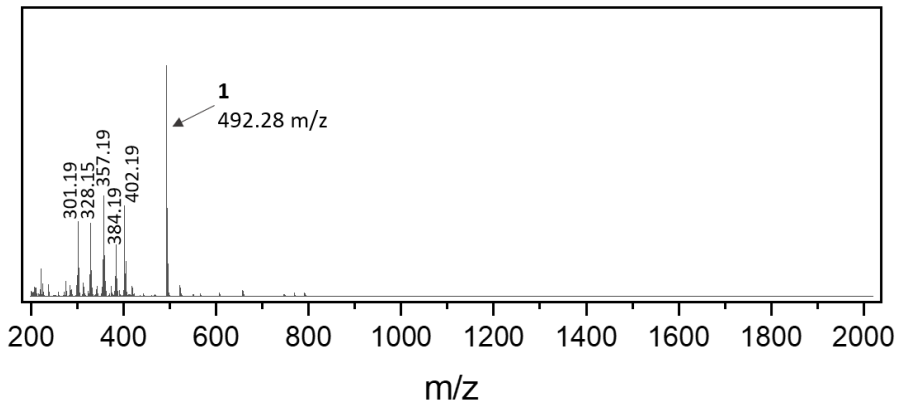



Fig. S 10. LIFDI mass spectrum of **1** (m/z exp.492.2822; calc. 492.2847). Other observed signals induced by the analytical instrument were assigned to the following fragments: 1-cod (m/z 384.1897); 1-Cp* (m/z 357.2033); 1-2hex (m/z 328.1658); 1-cod-hex (m/z 301.1448).

## IR spectroscopic data of 1

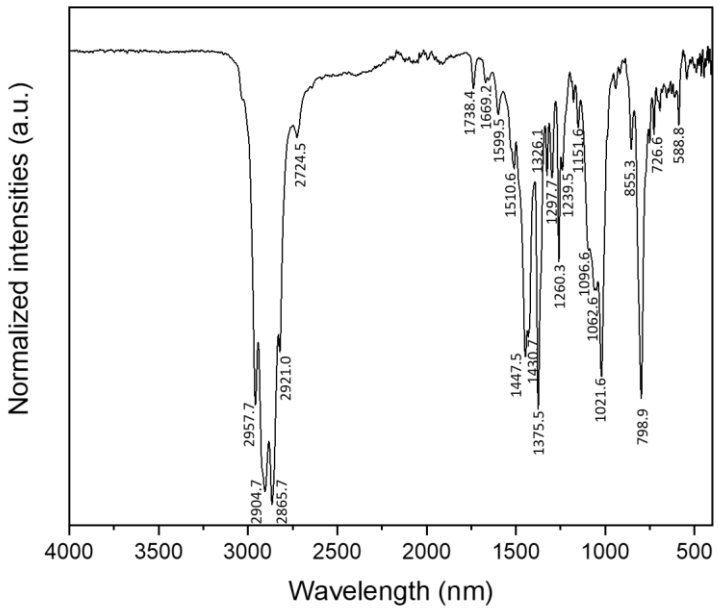



Fig. S 11. ATR IR spectrum of **1**.

## Calculated frequencies (BP86-D3/def2-svp) for 1

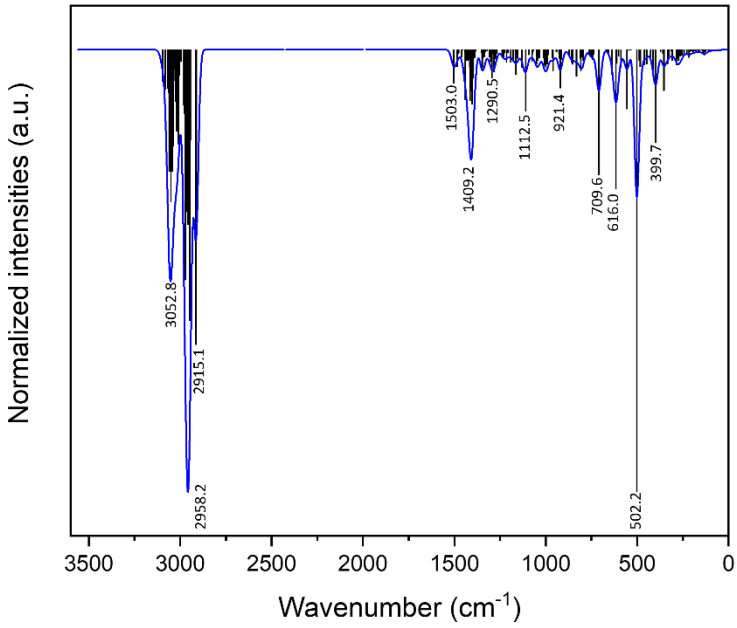



Fig.S 12. Calculated frequencies of **1** on the BP86-D3/def2-svp level of theory.

### UV-vis spectroscopic data of 1

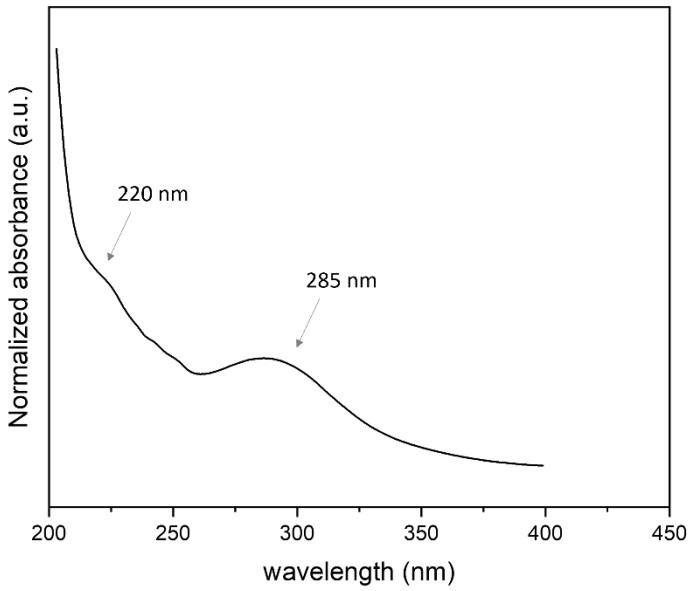
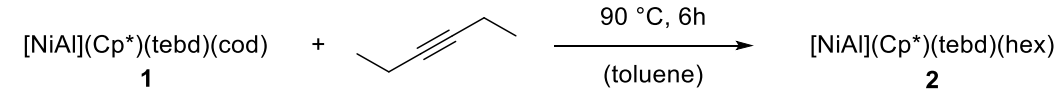


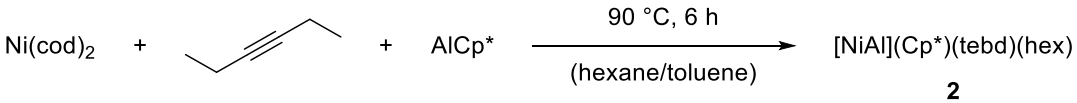

Fig. S 13. UV-vis spectrum of **1** in *n*-hexane with absorption maxima at 220 nm and 285 nm.

## [NiAl](Cp*)(tebd)(hex) (**2**)

### Synthesis procedure of 2




Procedure A: **1** (52 mg, 0.105 mmol, 1.0 eq.) was suspended in 1.5 mL toluene and 3-hexyne (0.80 mL, 0.80 mmol, 7.6 eq) was added as a 1 M solution in toluene. The reaction was stirred for 6 h at 90 °C to give a dark red solution.




Procedure B: $Ni(cod)_2$ (50 mg, 0.182 mmol, 1.0 eq.) and AlCp* (29 mg, 0.179 mmol, 1.0 eq.) were suspended in 3 mL hexane and 3-hexyne (1.54 mL, 1.54 mmol, 8.6 eq) was added as a 1 M solution in toluene to give a red solution within seconds. The reaction was stirred for 6 h at 90 °C to give a dark red solution.
*Note: Due the instability in vacuo and the high solubility in unpolar solvents,* ***2*** *could not be isolated.*

**$^{1}$H NMR** (400 MHz, 293 K, $C_6D_{12}$): δ (ppm) = 2.82 – 2.49 (m, 4H, $CH_{2,Acetylene}$), 2.23 – 2.10 (m, 4H, $CH_{2,butadiene}$), 2.04 – 2.01 (m, 4H, $CH_{2,Acetylene}$), 1.99 (s, 15H, $C_5Me_5$), 1.15 (t, $^{3}J$ = 7.4 Hz, 6H, $CH_{3,Acetylene}$), 0.98 (dt, $^{3}J$ = 7.5 Hz, 12H, $CH_{3,Acetylene}$).

**$^{13}$C NMR** (101 MHz, 293 K, $C_6D_{12}$): δ (ppm) = 132.2 ($C{\equiv}C_{Acetylene}$), 122.7 ($C{=}C_{butadiene}$), 113.9 ($C_5Me_5$), 27.0 ($CH_{2,butadiene}$), 21.8 ($CH_{2,Acetylene}$), 19.9 ($CH_{2,butadiene}$), 16.6 ($CH_{3,butadiene}$), 16.5 ($CH_{3,butadiene}$), 16.0 ($CH_{3,Acetylene}$), 10.6 ($C_5Me_5$).

**IR (ATR, neat, cm$^{-1}$):** 2961, 2927, 2869, 1825, 1576, 1453, 1374, 1304, 1260, 1055, 1021, 804, 716, 678, 527, 508.

**HRMS (LIFDI, toluene/hexane):** m/z calcd for $C_{52}H_{40}NiAl$: 466.2685; found: 466.2684.

**UV/Vis** (*n*-hexane): $\lambda_{max}$ = 375, 315, 215 nm.

## NMR spectroscopic data of 2

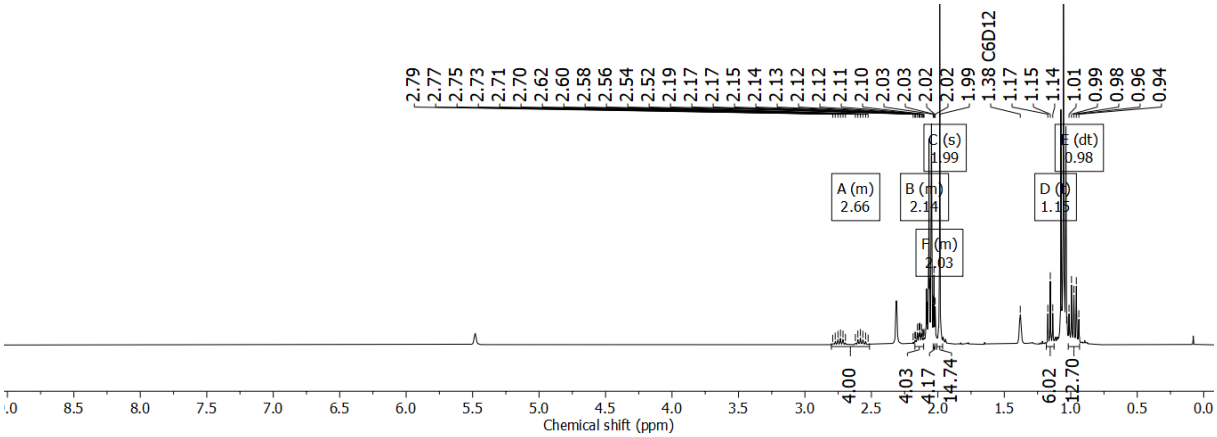



Fig. S 14. $^{1}$H NMR spectrum of [NiAl](Cp*)(tebd)(hex) (**2**) in cyclohexane-$d_{12}$. Impurities: cod (5.50 and 2.23 ppm) due to *in-situ* NMR measurement.

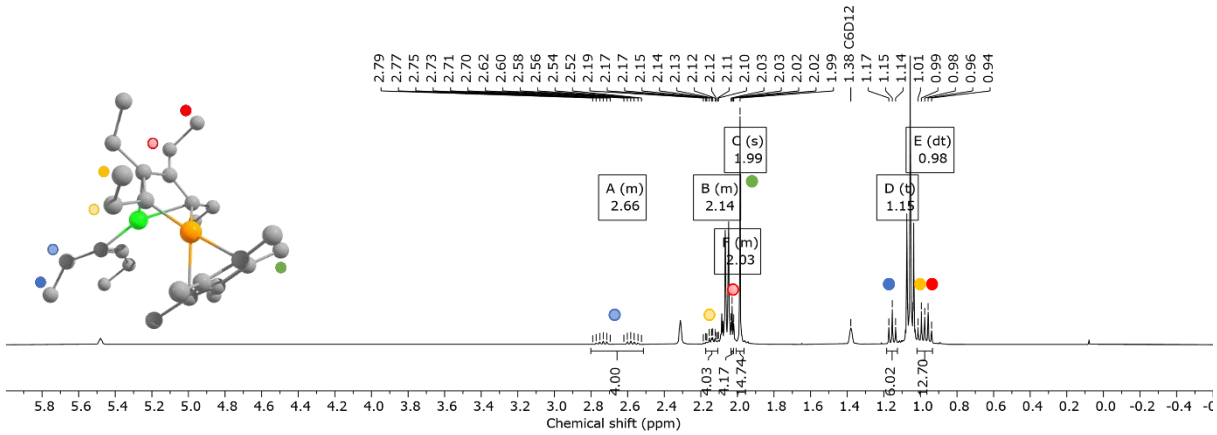



Fig. S 15. $^{1}$H NMR spectrum of **2** in cyclohexane-$d_{12}$ with assignment.

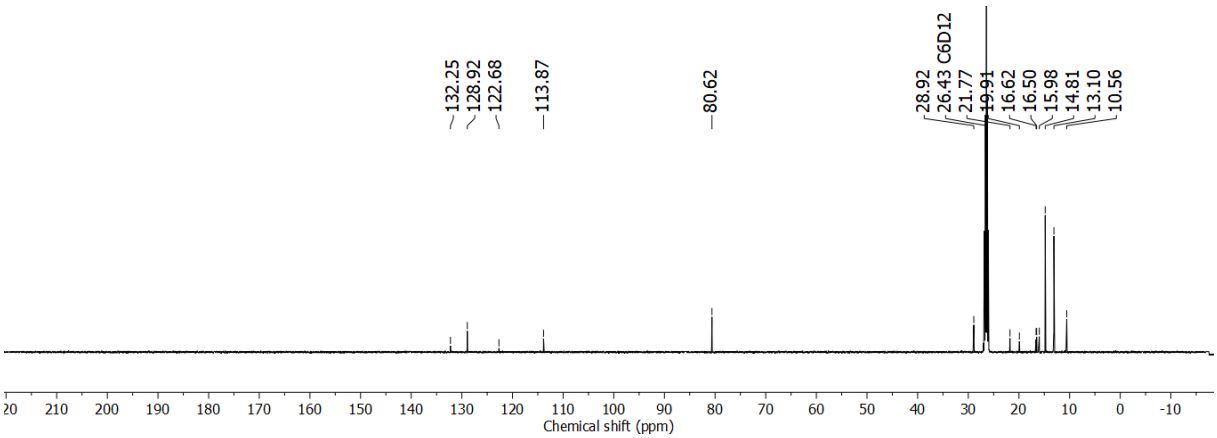



Fig. S 16. $^{13}$C NMR spectrum of **2** in cyclohexane-$d_{12}$.

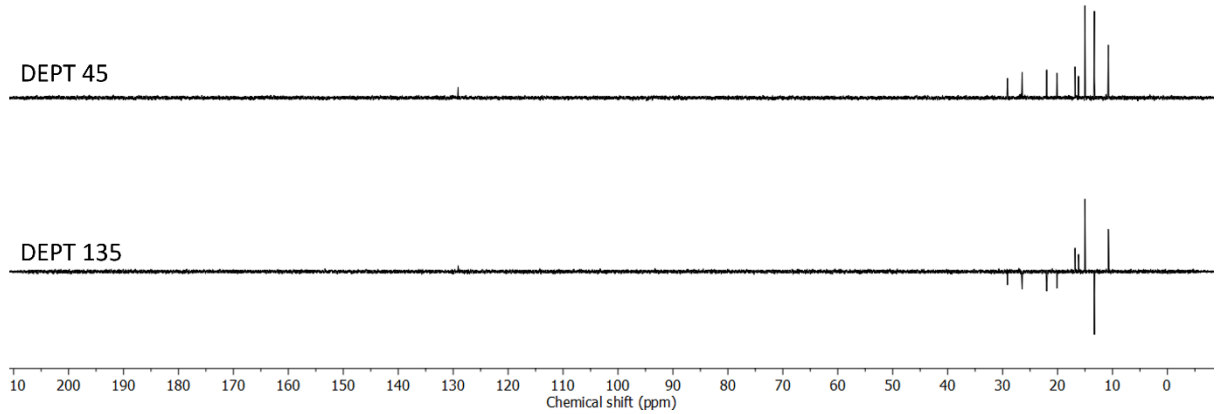



Fig. S 17. DEPT 135 and DEPT 45 NMR spectrum of **2** in cyclohexane-$d_{12}$. DEPT135: Negative signals refer to $CH_2$ groups, whereas positive signals are assigned as CH or $CH_3$ groups.

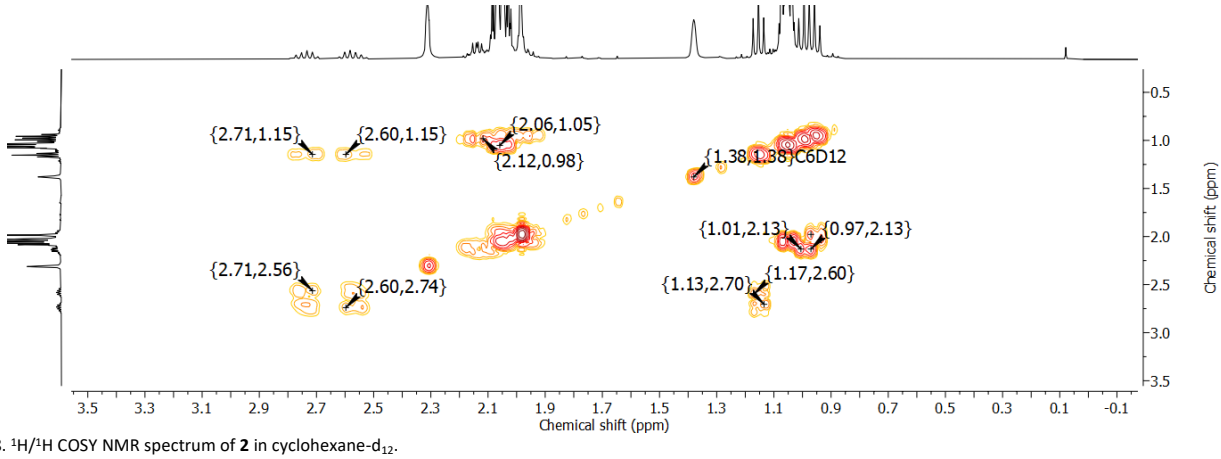



Fig.S 18. $^1H/^1H$ COSY NMR spectrum of **2** in cyclohexane-$d_{12}$.

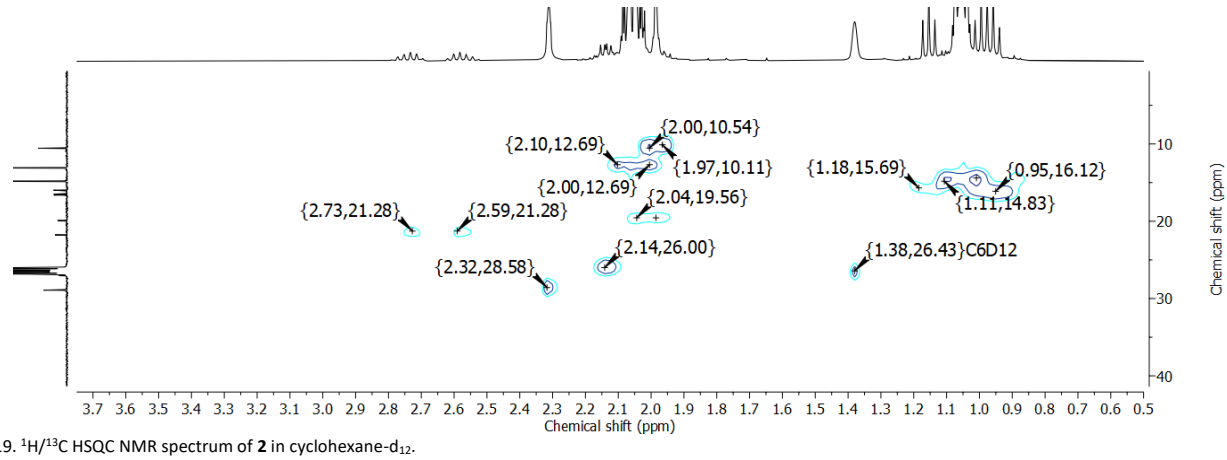



Fig. S 19. $^1H/^{13}C$ HSQC NMR spectrum of **2** in cyclohexane-$d_{12}$.

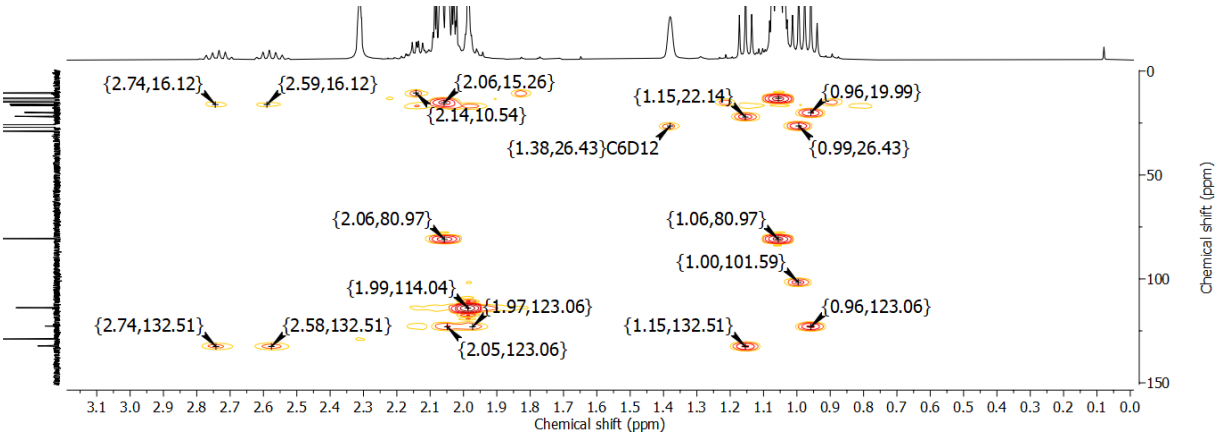



Fig. S 20. $^{1}H/^{13}C$ HMBC NMR spectrum of **2** in cyclohexane-$d_{12}$.

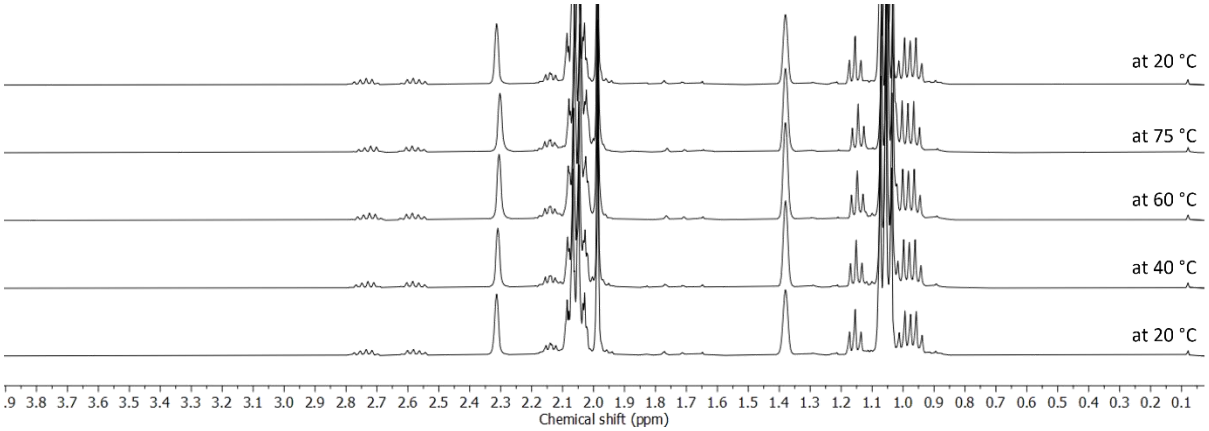



Fig. S 21. High temperature $^{1}H$ NMR studies of **2** in cyclohexane-$d_{12}$.

## Mass spectrometric data of 2

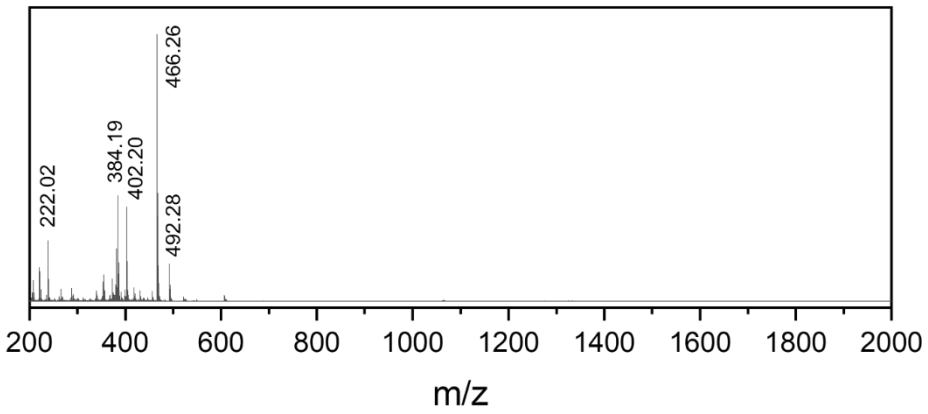



Fig. S 22. LIFDI mass spectrum of **2** (exp. 466.2684; calc. 466.2683 m/z). Other observed signals: 2-hex (m/z 384.1902), **1** (m/z 492.2840), 2-hex-AlCp* (m/z 222.0186).

## IR spectroscopic data of 2

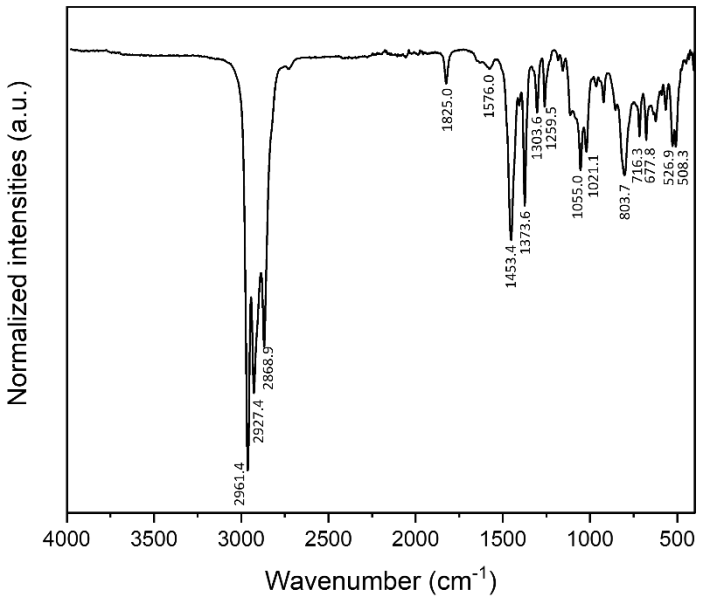



Fig. S 23. ATR-IR spectrum of **2** with the characteristic band at 1825.0 $cm^{-1}$ with relates to *side-on* coordinated hexyne.

## Calculated frequencies (BP86-D3/def2-svp) for 2

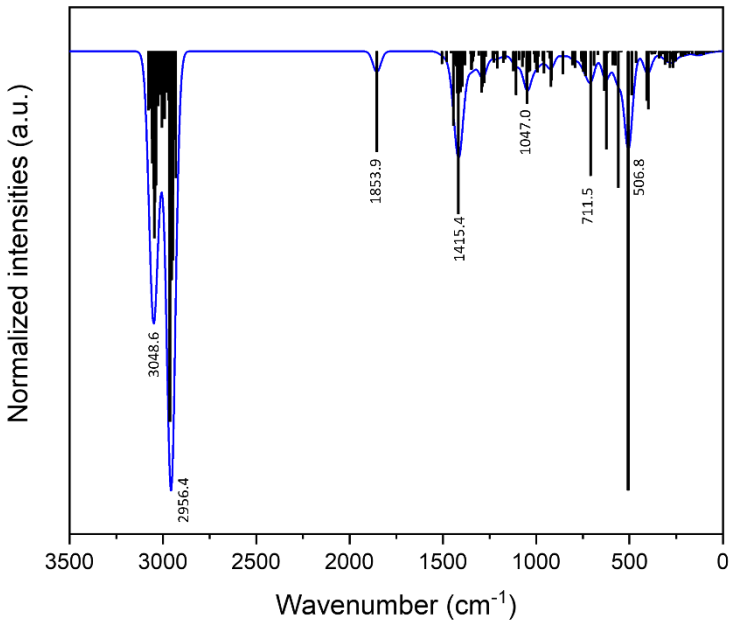



Fig. S 24. Calculated frequencies of **2** on the BP86-D3/def2-svp level of theory.

**UV-vis spectroscopic data of 2**

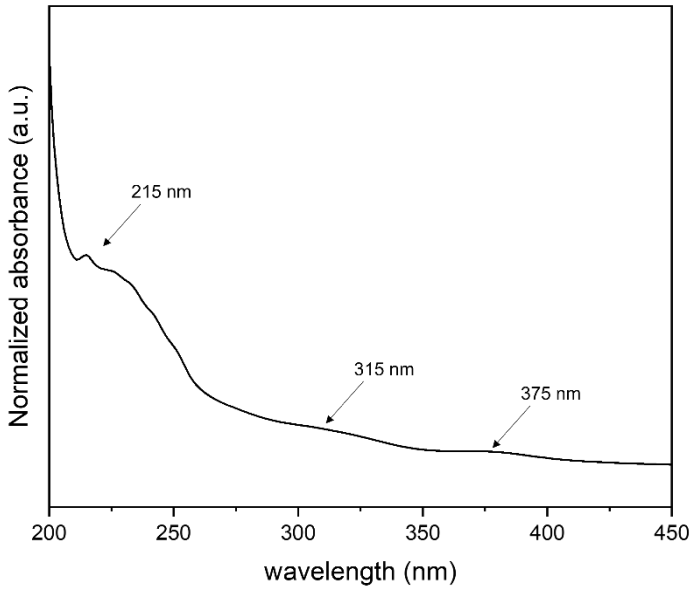
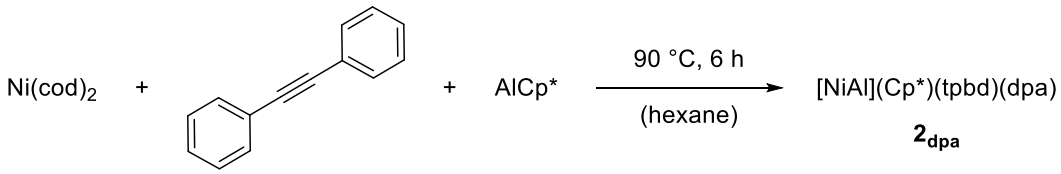



Fig. S 25. UV-vis spectrum of **2** in *n*-hexane with absorption maxima at 215 nm, 315 nm and 375 nm.

## [NiAl](Cp*)(tpbd)(dpa) (**2**$_{dpa}$)

**Synthesis procedure of 2$_{dpa}$**




$Ni(cod)_2$ (60 mg, 0.218 mmol, 1.0 eq.) and diphenylacetylene (310 mg, 1.74 mmol, 8.0 eq.) were suspended in 6 mL hexane to give a red solution after a few minutes. Subsequently, AlCp* (36 mg, 0.222 mmol, 1.0 eq.) was added and the reaction mixture was stirred at 90 °C for 6 h giving a red solution. After slowly cooling to room temperature, the obtained red precipitate was cannula filtered, washed with cold pentane (3 × 1.5 mL) and shortly exposed to vacuo to obtain a red powder (yield: 64 %). Single crystals suitable for X-ray analysis was either obtained by diffusion crystallization (toluene/hexane) or by storing a concentrated solution in toluene at -30 °C within one week.
*Note: **2**$_{dpa}$ is only stable with excess dpa. In addition, long exposure of **2**$_{dpa}$ to vacuo led to a black precipitate which is insoluble in common solvents.*

**$^1$H NMR** (400 MHz, 293 K, benzene-$d_6$): δ (ppm) = 7.76 (dt, $^3J$ = 8.2 Hz, 4H, *o*-C$H_{acetylene}$), 7.33 (d, $^3J$ = 7.0 Hz, 4H, *o*-C$H_{butadiene}$), 7.29 – 7.25 (m, 4H, *o*-C$H_{butadiene}$), 7.25 – 7.20 (m, 4H, *m*-C$H_{acetylene}$), 6.97 – 6.93 (m, 4H, *m*-C$H_{butadiene}$), 6.89 – 6.84 (m, 2H, *p*-C$H_{butadiene}$), 6.80 – 6.74 (m, 4H, *p*-C$H_{acetylene}$, *m*-C$H_{butadiene}$), 6.63 (tt, $^3J$ = 7.3 Hz, 2H, *p*-C$H_{butadiene}$), 1.65 (s, 15H, $C_5Me_5$).

**$^{13}$C NMR** (101 MHz, 293 K, benzene-$d_6$): δ (ppm) = 146.4 (C=C$_{butadiene}$), 141.0 (C=C$_{butadiene}$), 138.6 C$_{Ph,butadiene}$), 135.3 (C$_{Ph,Aceytylene}$), 134.2 (C≡C$_{Acetylene}$), 131.5 (*o*-C$_{Ph,butadiene}$), 131.1 (*o*-C$_{Ph,butadiene}$), 130.0 (*o*-C$_{Ph,Acetylene}$), 128.6 (*m*-C$_{Ph,Acetylene}$), 127.3 (*m*-C$_{Ph,butadiene}$), 127.0 (*p*-C$_{Ph,Acetylene}$, *m*-C$_{Ph,butadiene}$), 126.3 (*p*-C$_{Ph,butadiene}$), 123.9 (*p*-C$_{Ph,butadiene}$), 115.2 ($C_5$Me$_5$), 10.3 ($C_5Me_5$).

**IR (ATR, neat, cm$^{-1}$):** 3058, 2917, 1812, 1592, 1485, 1440, 1400, 1269, 1175, 1070, 1026, 911, 758, 690, 646, 562, 509.

**HRMS (LIFDI, toluene):** m/z calcd for $C_{52}H_{45}NiAl$: 754.2690; found: 754.2692.

**UV/Vis** (*n*-hexane): $\lambda_{max}$ = 215, 280, 330 nm.

## NMR spectroscopic data of $2_{dpa}$

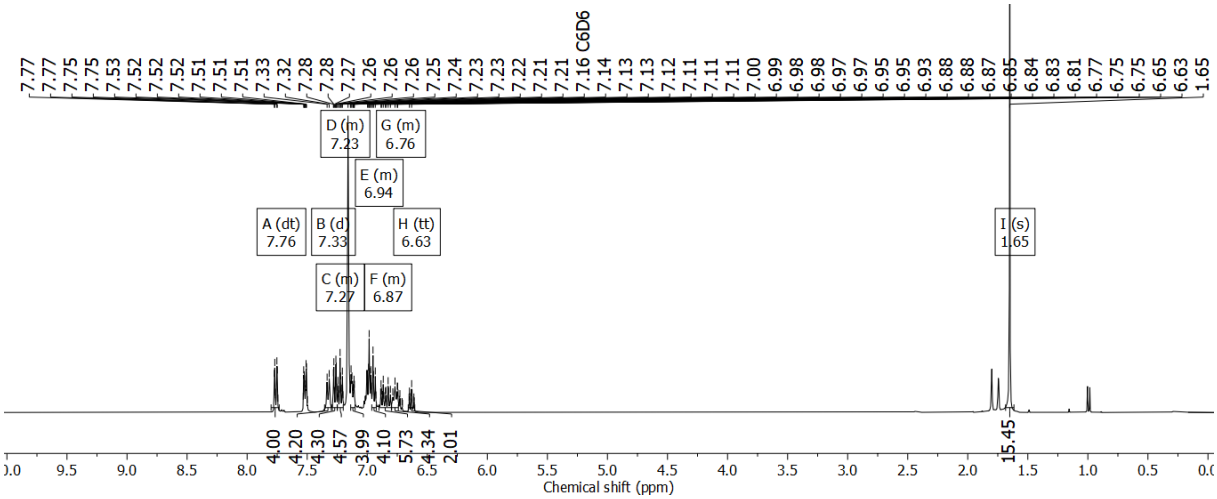



Fig. S 26. $^{1}$H NMR spectrum of [NiAl](Cp*)(tpbd)(dpa) (**$2_{dpa}$**) in benzene-$d_6$. Impuritie (ppm): dpa (7.52 (m) and 6.98 ppm (m)), $dpa_3$ (trimerized dpa) (7.12 (m) and 6.72 ppm (m)) and Cp* (1.80 (s), 1.74 (s), 0.99 ppm (d)).

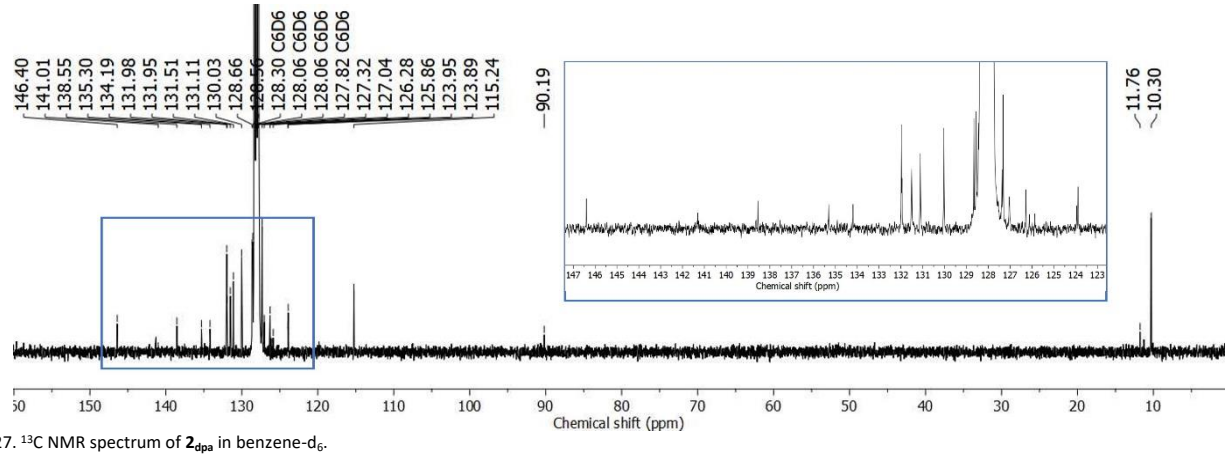



Fig. S 27. $^{13}$C NMR spectrum of **$2_{dpa}$** in benzene-$d_6$.

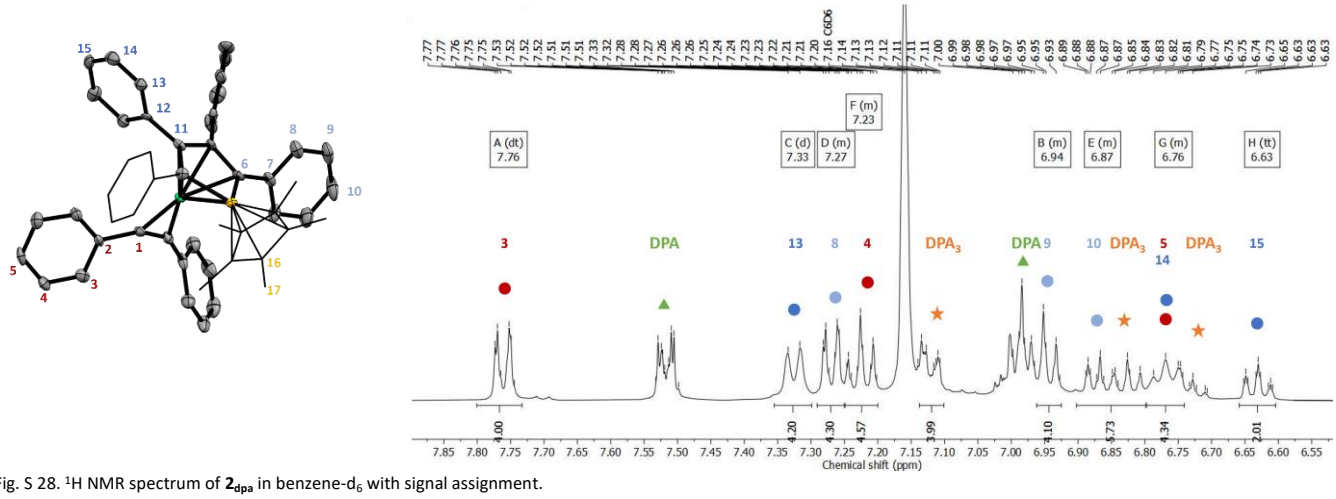



Fig. S 28. $^{1}$H NMR spectrum of **$2_{dpa}$** in benzene-$d_6$ with signal assignment.

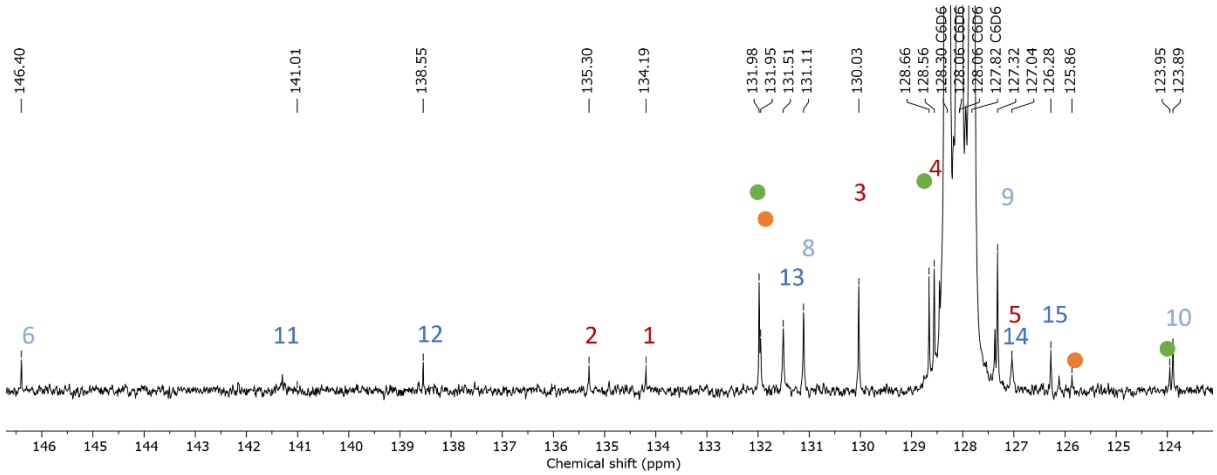



Fig.S 29. Enlarged $^{13}C$ NMR spectrum of $\mathbf{2}_{dpa}$ in benzene-$d_6$ with signal assignment. Orange dots refer to trimerized dpa (hexaphenylbenzene) and green dots are assigned to free dpa.

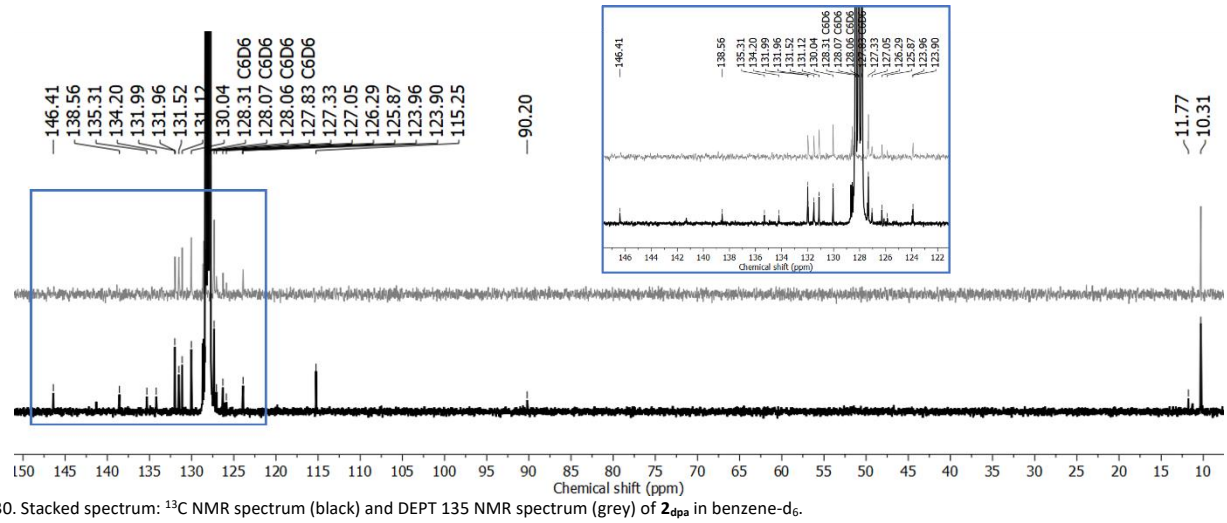



Fig. S 30. Stacked spectrum: $^{13}C$ NMR spectrum (black) and DEPT 135 NMR spectrum (grey) of $\mathbf{2}_{dpa}$ in benzene-$d_6$.

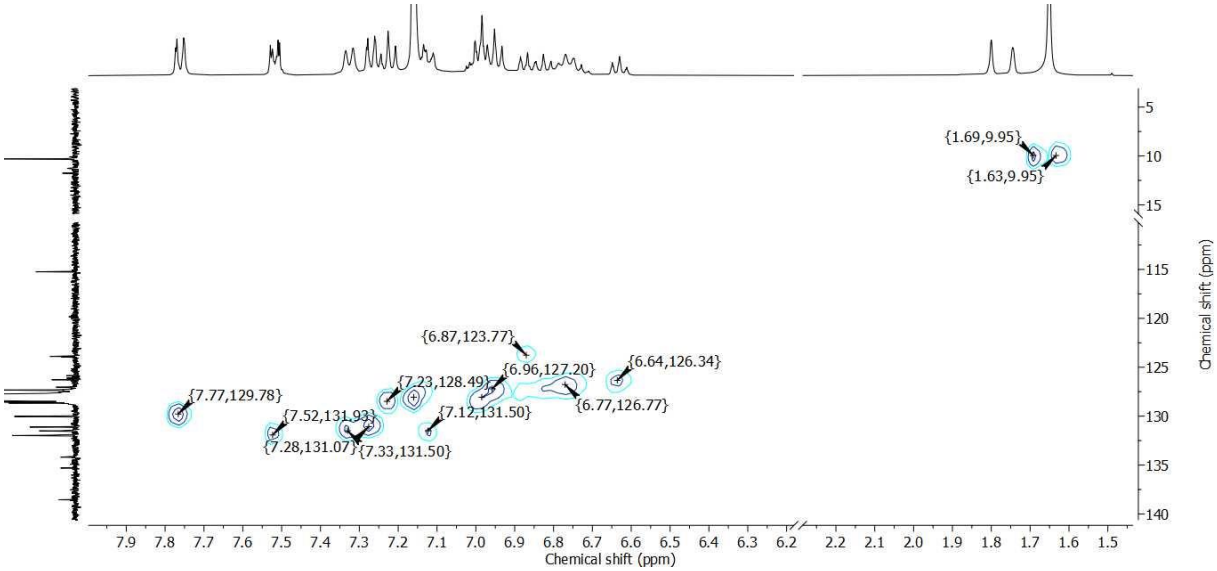



Fig. S 31. $^{1}H/^{13}C$ HSQC NMR spectrum of $\mathbf{2}_{dpa}$ in benzene-$d_6$.

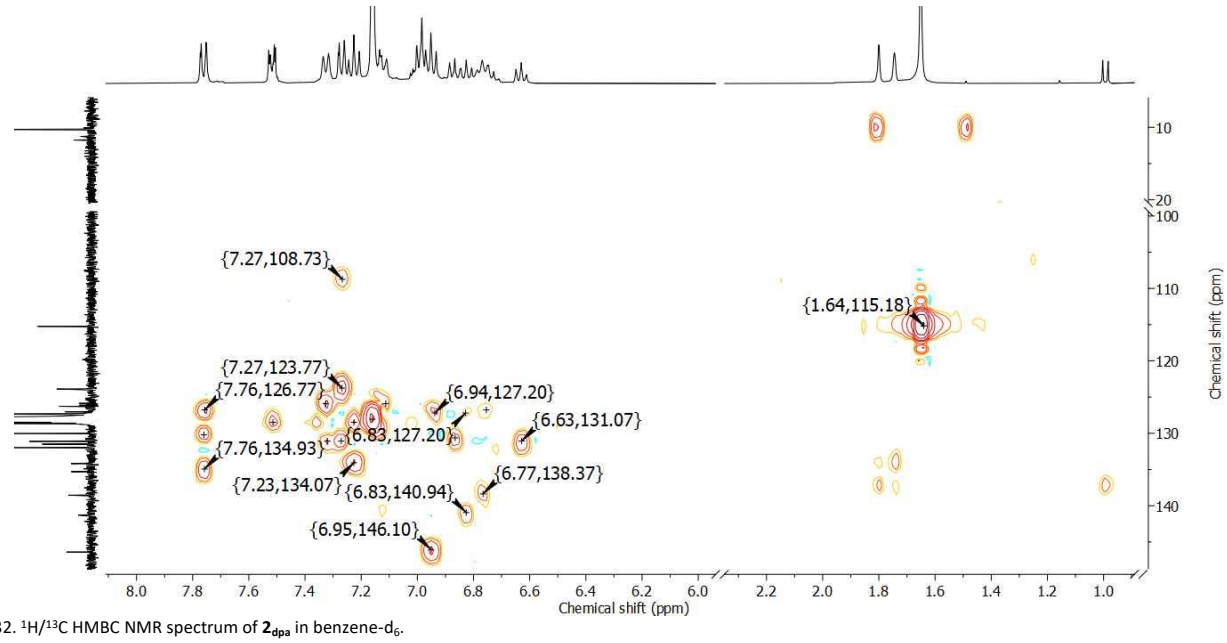



Fig. S 32. $^{1}H/^{13}C$ HMBC NMR spectrum of $\mathbf{2}_{dpa}$ in benzene-$d_6$.

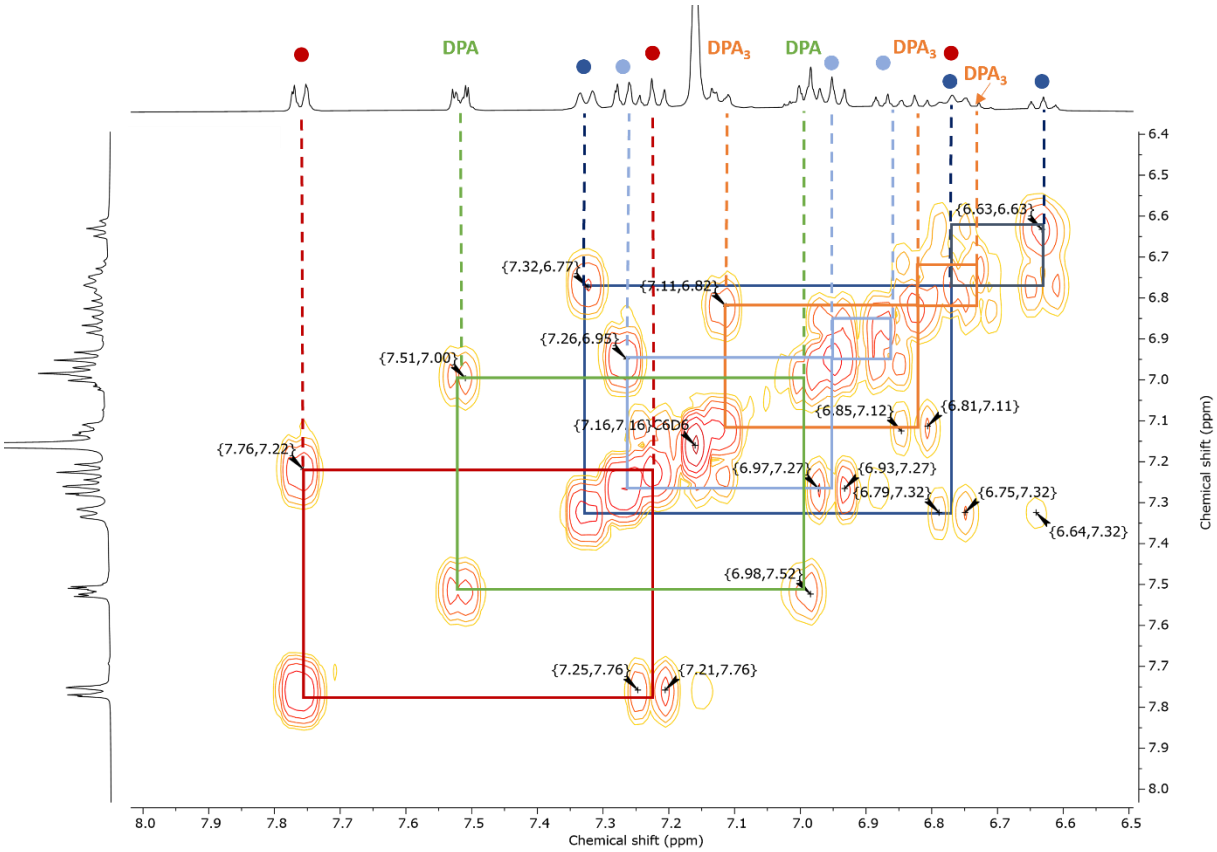



Fig. S 33. $^{1}H/^{1}H$ COSY NMR spectrum of $\mathbf{2}_{dpa}$ in benzene-$d_6$. $DPA_3$ relates to trimerized dpa (hexaphenylbenzene).

## Mass spectrometric data of $2_{dpa}$

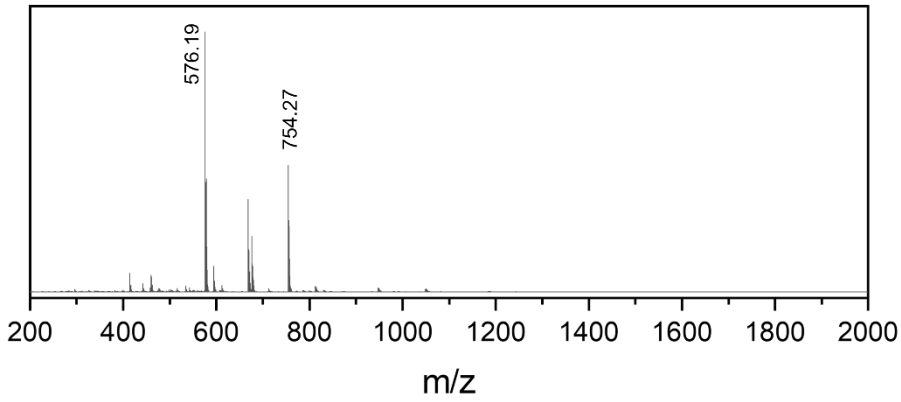



Fig. S 34. LIFDI mass spectrum of **$2_{dpa}$** (m/z exp.754.2690; calc. 754.2692). Other observed signals induced by the analytical instrument were assigned to the following fragments: $2_{dpa}$ -dpa (m/z 576.1886).

## IR spectroscopic data of $2_{dpa}$

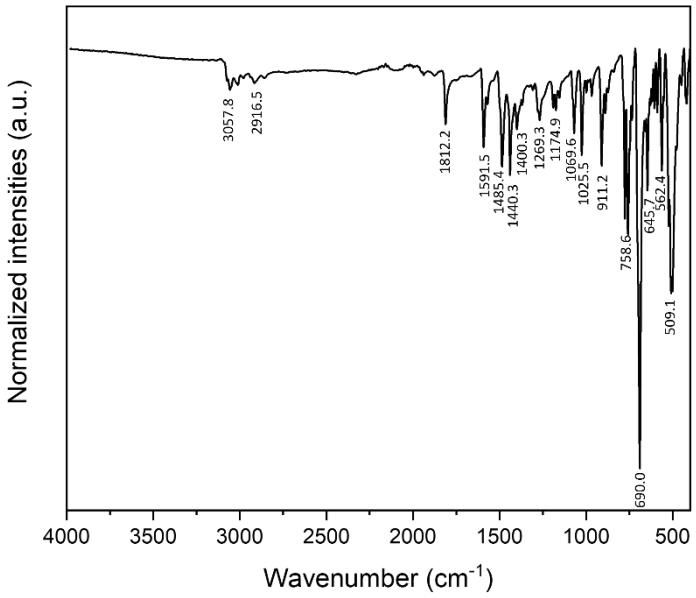



Fig. S 35. ATR IR spectrum of **$2_{dpa}$** with the characteristic band at 1812.2 $cm^{-1}$ which is assigned to *side-on* coordinated dpa.

## Calculated frequencies (BP86-D3/def2-svp) for $2_{dpa}$

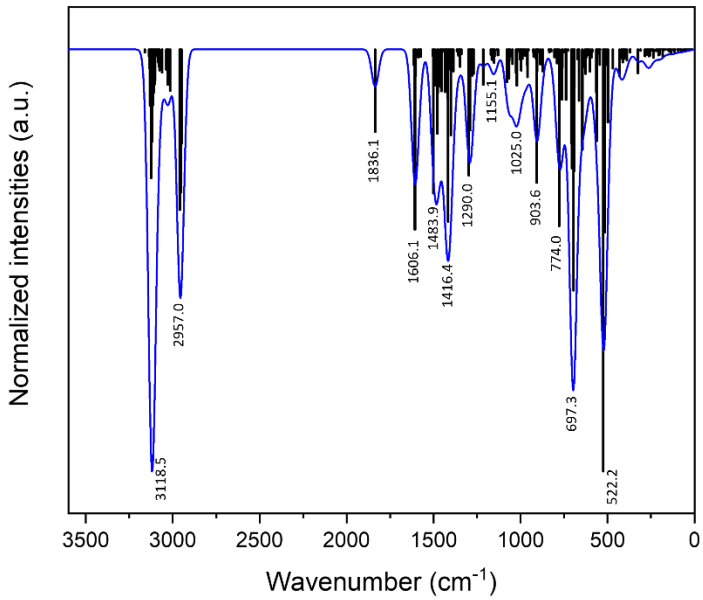



Fig. S 36. Calculated frequencies of $\mathbf{2}_{dpa}$ on the BP86-D3/def2-svp level of theory.

## UV-vis spectroscopic data of $2_{dpa}$

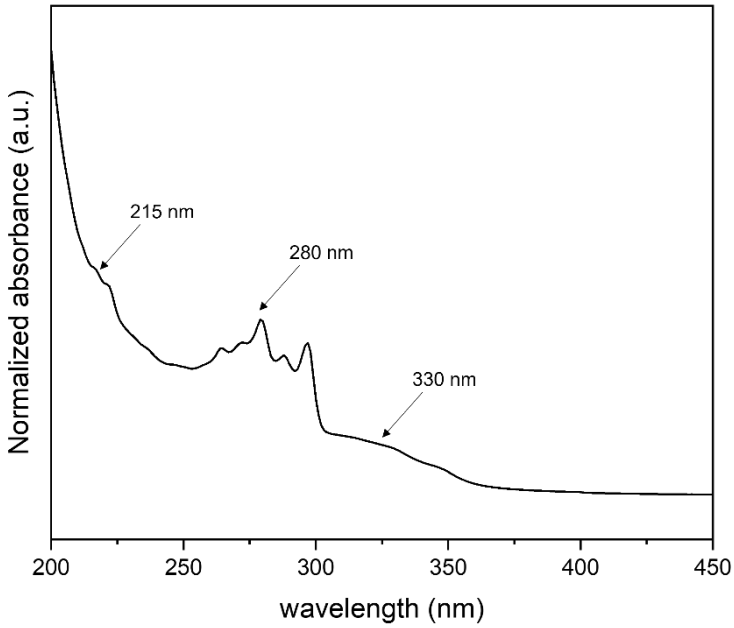
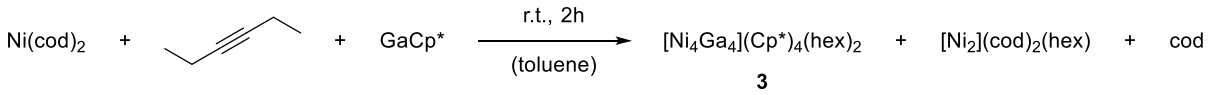



Fig. S 37. UV-vis spectrum of $\mathbf{2}_{dpa}$ in *n*-hexane with absorption maxima at 215, 280 and 330 nm.

## $[Ni_4Ga_4](Cp^*)_4(hex)_2$ (**3**)

### Synthesis procedure of 3




$Ni(cod)_2$ (50 mg, 0.182 mmol, 1.0 eq.) and 3-hexyne (0.09 mL, 1 M solution in toluene, 0.180 mmol, 0.5 eq) were dissolved in toluene giving a dark red solution within seconds. Subsequently, GaCp* (0.18 mL, 0.180 mmol, 1.0 eq.) was added as a 1 M solution in toluene and stirred for two hours at ambient temperature to obtain a brown solution. Spectroscopic yield with cyclohexane as internal standard: 19%.
*Note: Long exposure of **3** to vacuo led to an insoluble black precipitate. In solution, however, it is stable for several days when stored at -30 °C.*

**$^1$H NMR** (400 MHz, 298 K, toluene-$d_8$): δ (ppm) = 2.70 (s, 8H, C$H_{2,hex}$), 1.98 (s, 60H, $C_5Me_5$), 1.33 (s, 12H, C$H_{3,hex}$).

**$^{13}$C NMR** (101 MHz, 298 K, toluene-$d_8$): δ (ppm) = 134.8 (C≡$C_{Acetylene}$), 113.6 ($C_5Me_5$), 22.9 ($CH_{2,Acetylene}$) 16.6 ($CH_{3,Acetylene}$), 10.90 ($C_5Me_5$).

**IR (ATR, neat, cm$^{-1}$)**: 2959, 2906, 2864, 2822, 2725, 1739, 1670, 1600, 1510, 1448, 1375, 1260, 1240, 1152, 1063, 1022, 856, 800, 589

**HRMS (LIFDI, toluene):** m/z calcd for $C_{52}H_{80}Ni_4Ga_4$: 1218.0627; found: 1218.0633.

### NMR spectroscopic data of 3

Table S 1. Overview of the chemical shifts of different compounds in ppm (298K, 400 MHz, toluene-$d_8$). bs means broad singlet.

| Compound | 1H NMR shifts | 13C NMR shifts |
|---|---|---|
| **$[Ni(cod)_2]$** | 4.26 (s, CH), 2.05 (s, $CH_2$) | 90.1, 31.2 |
| **3-hexyne** | 2.01 (q, $CH_2$), 1.01 (t, $CH_3$) | 81.4, 15.0, 13.2 |
| **GaCp*** | 1.93 (s, $CH_3$) | 113.89, 10.24 |
| **$[Ni_4Ga_4](Cp^*)_4(hex)_2$** | 2.70 (bs, $CH_{2,hex}$), 1.97 (s, $CH_{3,\ Cp^*}$), 1.33 (bs, $CH_{3,\ hex}$) | 134.8, 113.6, 22.9, 16.6, 10.9 |
| **$[Ni_2](cod)_2(hex)$** | 5.25 (s, $CH_{cod}$), 2.60 (q, $CH_{2,\ hex}$), 2.06 (s, $CH_{2,cod}$), 1.17 (t, $CH_{3,\ hex}$) | 129.8, 93.42, 31.04, 20.6, 15.0 |
| **cod** | 5.54 (s, CH), 2.21 (s, $CH_2$) | 129.1, 28.8 |

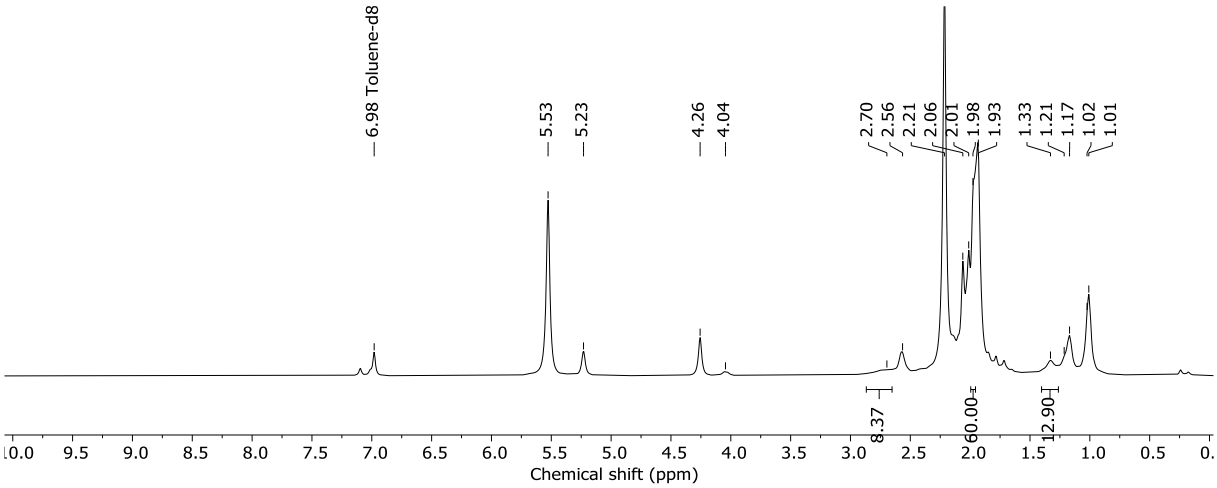



Fig. S 38. $^{1}$H NMR spectrum of $[Ni_4Ga_4](Cp^*)_4(hex)_2$ (**3**) in toluene-$d_8$.

Besides the product signals, the $^{1}$H and the $^{13}$C NMR spectrum exhibits signals of the starting materials $Ni(cod)_2$, 3-hexyne and GaCp* as well as signals of the side products $Ni_2cod_2hex$ and cod. The assignment is depicted below. Indeed, the isolation failed so far caused by potential equilibrium as it is known for $Ni_2cod_2hex$.

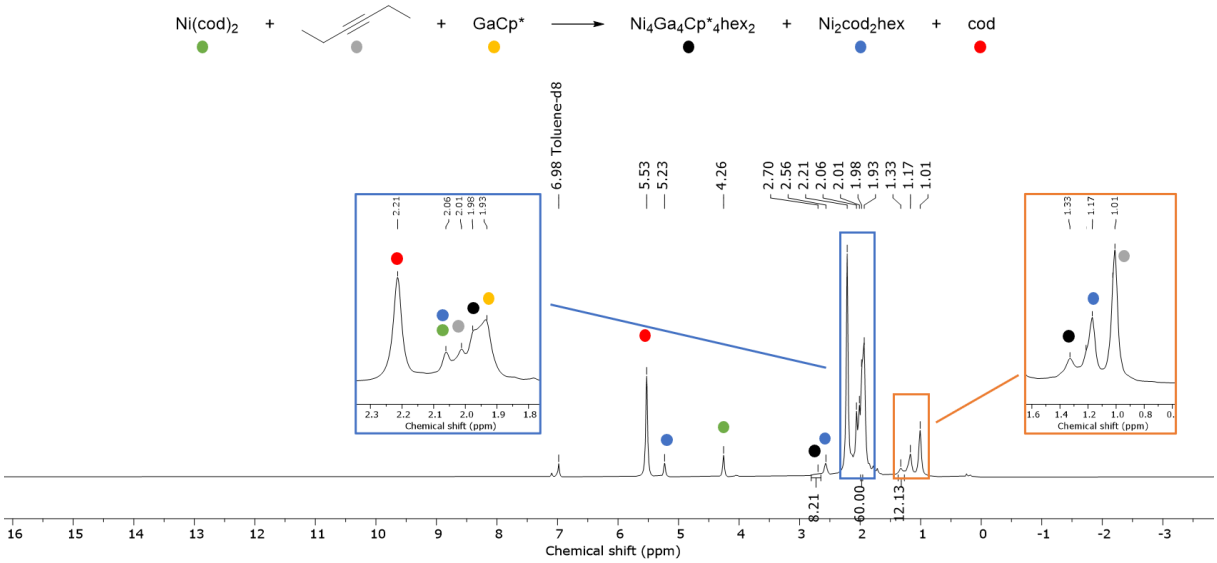



Fig. S 39. $^{1}$H NMR spectrum of the synthesis of **3** (black) in toluene-$d_8$ with assignments of the starting materials as well as side products.

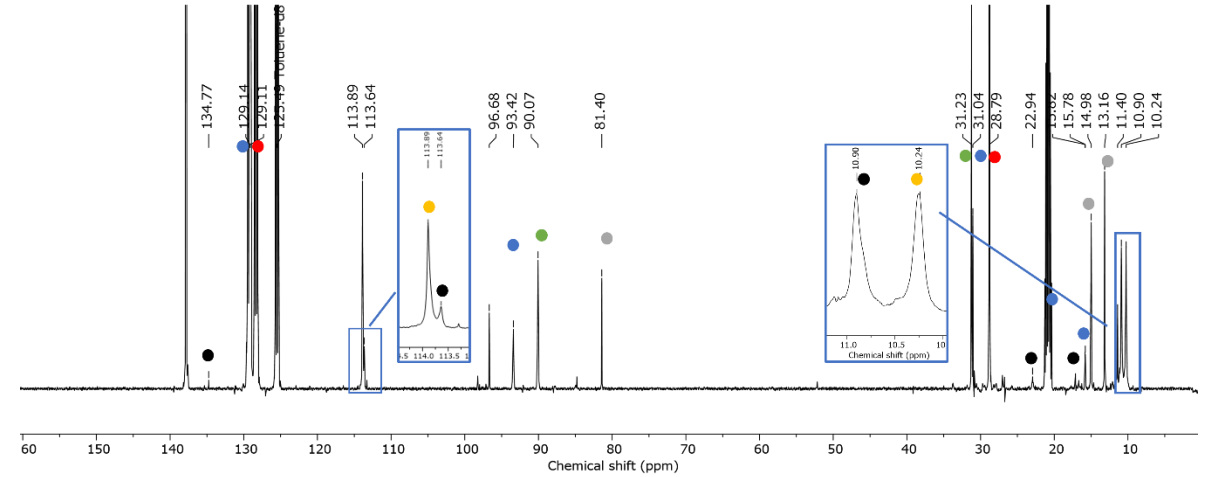



Fig. S 40. $^{13}$C NMR spectrum of **3** (black) in toluene-$d_8$ with assignments of the starting materials as well as side products.

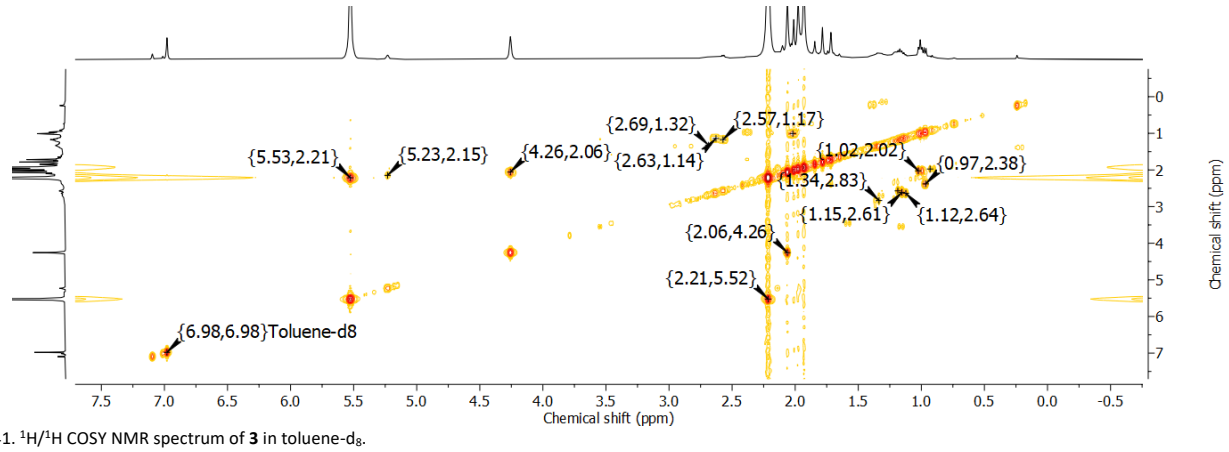



Fig. S 41. $^{1}H/^{1}H$ COSY NMR spectrum of **3** in toluene-$d_8$.

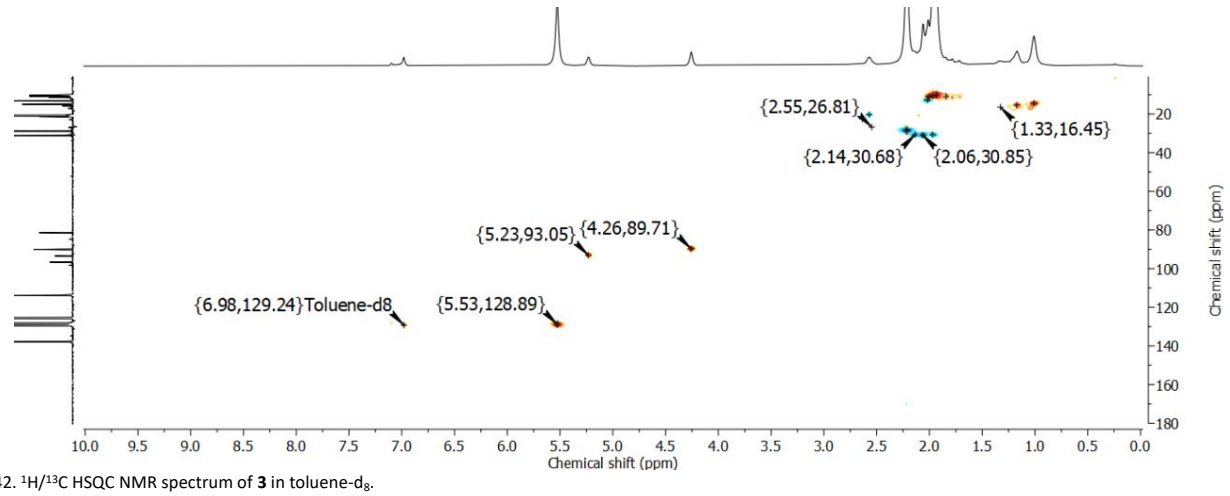



Fig. S 42. $^{1}H/^{13}C$ HSQC NMR spectrum of **3** in toluene-$d_8$.

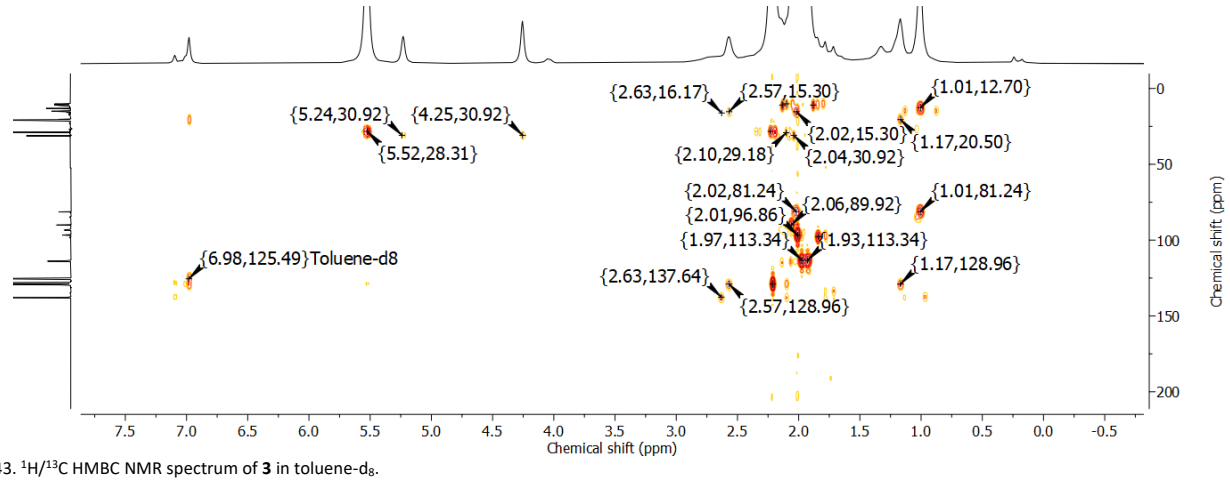



Fig. S 43. $^{1}H/^{13}C$ HMBC NMR spectrum of **3** in toluene-$d_8$.

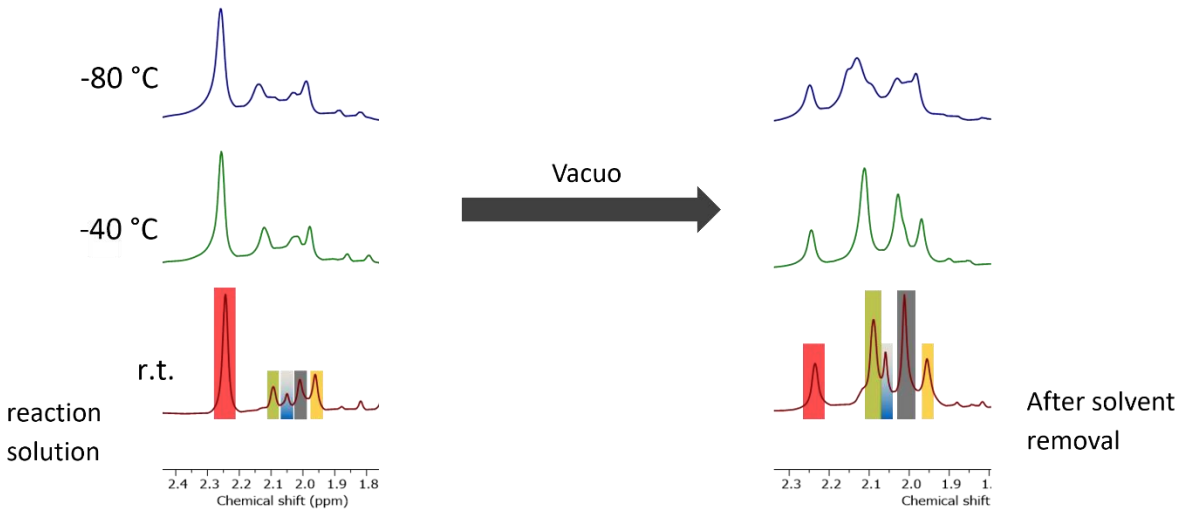



Fig. S 44. Low temperature NMR studies of **3** in toluene-$d_8$. Left: Original reaction solution, right: after short exposure to vacuo showing the decrease of volatile components as cod (red), GaCp* (yellow), hexyne and $Ni_2cod_2hex$ (light grey mixed with blue). Dark grey and green highlighted signals are referred to **3** and $Ni(cod)_2$, respectively.

## Mass spectrometric data of 3

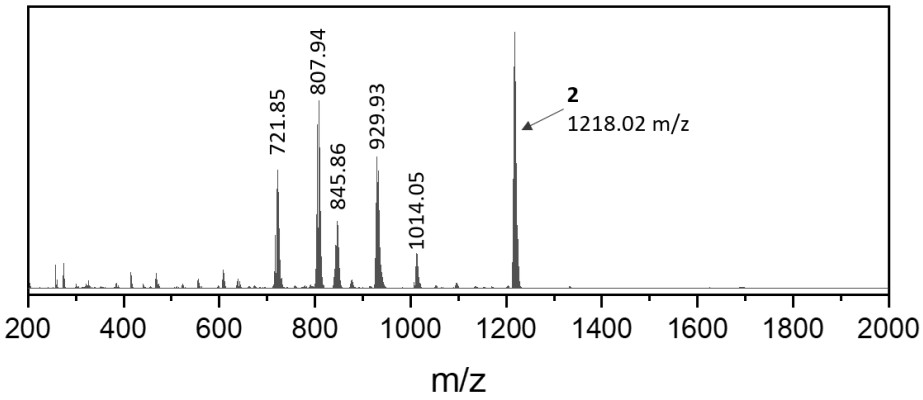



Fig. S 45. LIFDI mass distribution of **3** measured on an Exactive Orbitrap System by Thermo Fischer. 1218.0633: $[Ni_4Ga_4](Cp^*)_4(hex)_2$ (calc.: 1218.0627 m/z); 1014.05: 3-GaCp*; 929.93: 3-GaCp*-hex; 845.86: 3-GaCp*-2hex-2H; 807.94: 3-2GaCp*; 721.85: 3-2GaCp*-hex-4H.

**IR spectroscopic data of 3**

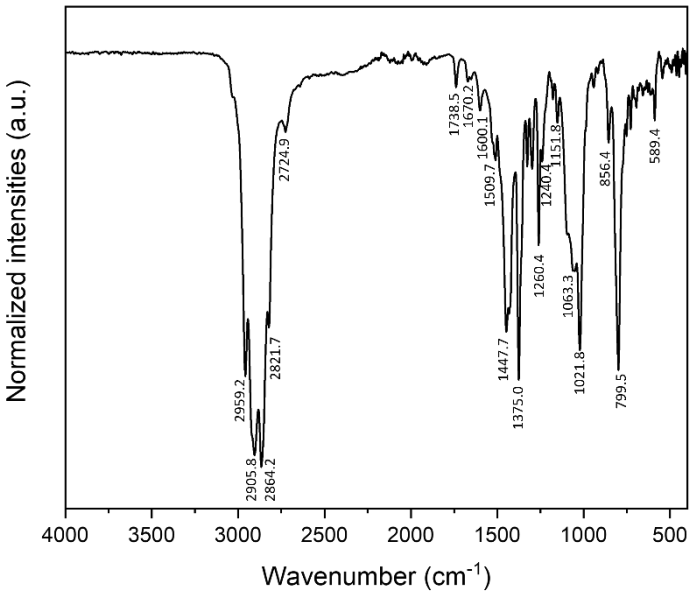



Fig. S 46. ATR IR spectrum of **3** with characteristic band at 1738.5 $cm^{-1}$ assuming a *side-on* coordinated hexyne.

## Calculated frequencies (BP86-D3/def2-svp) for 3

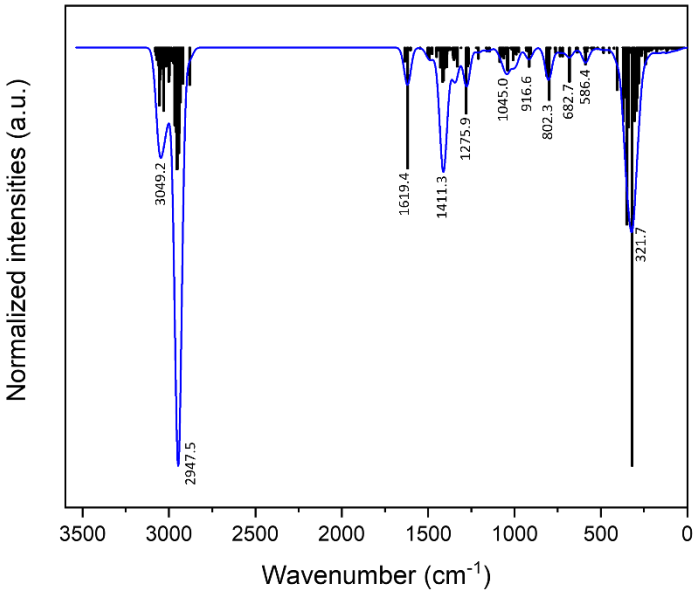



Fig. S 47. Calculated frequencies of **3** on the BP86-D3/def2-svp level of theory.

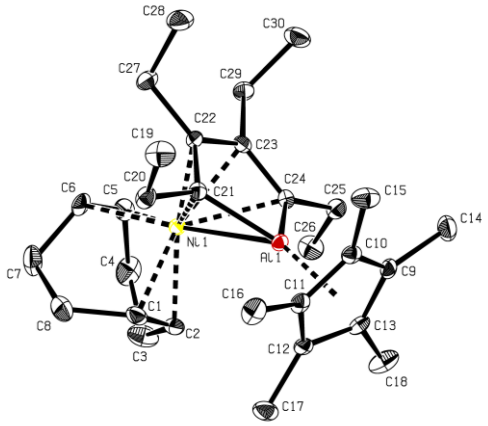
## Crystallographic data

### X-ray Crystallographic Details

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), a TXS rotating anode with $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a Helios optic using the APEX3 software package.[1] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[2] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[2] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps and were refined against all data using SHELXL-2014 in conjunction with SHELXLE.[3,4,5] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme.[3] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[6] A split layer refinement was used for disordered groups and additional SIMU, DELU, RIGU, ISOR, SAME and SADI restraints and EADP constraints were employed to ensure convergence within chemically reasonable limits, if necessary. Images of the crystal structures were generated with PLATON and Mercury.[7,8]

# Crystallographic data of 1

## CCDC 2133885



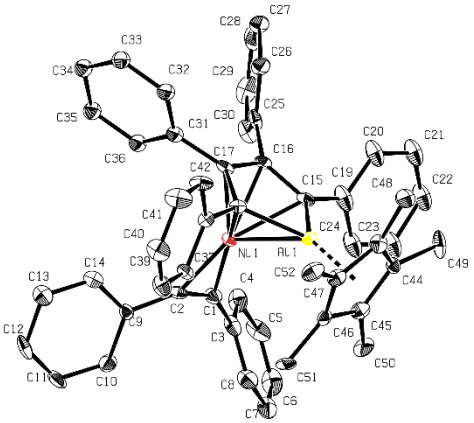

Diffractometer operator Patricia Heiss
scanspeed 2-10 s per frame
dx 37 mm
918 frames measured in 5 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_{30}H_{47}AlNi$ |
| $M_r$ | 493.36 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 17.885 (3), 9.5820 (15), 17.095 (2) |
| β (°) | 115.958 (5) |
| $V$ (Å$^3$) | 2634.1 (7) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| μ (mm$^{-1}$) | 0.79 |
| Crystal size (mm) | 0.21 × 0.19 × 0.16 |
| **Data collection** | |
| Diffractometer | Bruker D8 Venture Duo IMS |
| Absorption correction | Multi-Scan |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 27684, 5385, 4580 |
| $R_{int}$ | 0.052 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.625 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.072, 1.05 |
| No. of reflections | 5385 |
| No. of parameters | 477 |
| H-atom treatment | All H-atom parameters refined |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.44, −0.30 |

Computer programs: SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2018).

## Crystallographic data of $2_{dpa}$

### CCDC 2133886




Diffractometer operator Patricia Heiss
scanspeed 15 s per frame
dx 42 mm
3210 frames measured in 14 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_{118}H_{100}Al_2Ni_2$ |
| $M_r$ | 1689.35 |
| Crystal system, space group | Monoclinic, *Pn* |
| Temperature (K) | 100 |
| *a, b, c* (Å) | 14.305 (4), 15.217 (4), 21.403 (7) |
| *β* (°) | 105.807 (11) |
| *V* (Å$^3$) | 4483 (2) |
| *Z* | 2 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 0.49 |
| Crystal size (mm) | 0.13 × 0.11 × 0.10 |
| **Data collection** | |
| Diffractometer | Bruker D8 Venture TXS |
| Absorption correction | Multi-Scan |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 16085, 16085, 14960 |
| $R_{int}$ | 0.038 |
| (sin θ/λ)max (Å$^{-1}$) | 0.628 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.038, 0.090, 1.04 |
| No. of reflections | 16085 |
| No. of parameters | 1112 |
| No. of restraints | 2 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å−3) | 0.68, −0.41 |
| Absolute structure | No quotients, so Flack parameter determined by classical intensity fit |
| Absolute structure parameter | 0.102 (5) |

Computer programs: SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2018).

## References


[1] *APEX suite of crystallographic software*, APEX 3, Version 2015-5.2, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

[2] *SAINT*, Version 8.34A and *SADABS*, Version 2014/5, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.
[3] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
[4] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
[5] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281–1284
[6] *International Tables for Crystallography, Vol. C* (Ed.: A. J. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199).
[7] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, *65*, 148–155.
[8] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.* **2008**, *41*, 466–470.
[9] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881.
[10] S. Parsons, H. D. Flack, T. Wagner, *Acta Crystallogr. Sect. B* **2013**, *69*, 249–259.

## Additional Experimental Data

Please note: The formulas included in the mass spectrum only reveal the composition of the compounds, but have no information about bonding. Therefore, it could be possible that compounds which have dimerized acetylene are assigned as $hex_2$.

## Influences on Ni/Al cluster formation

### Influence of additive amount at 60 °C

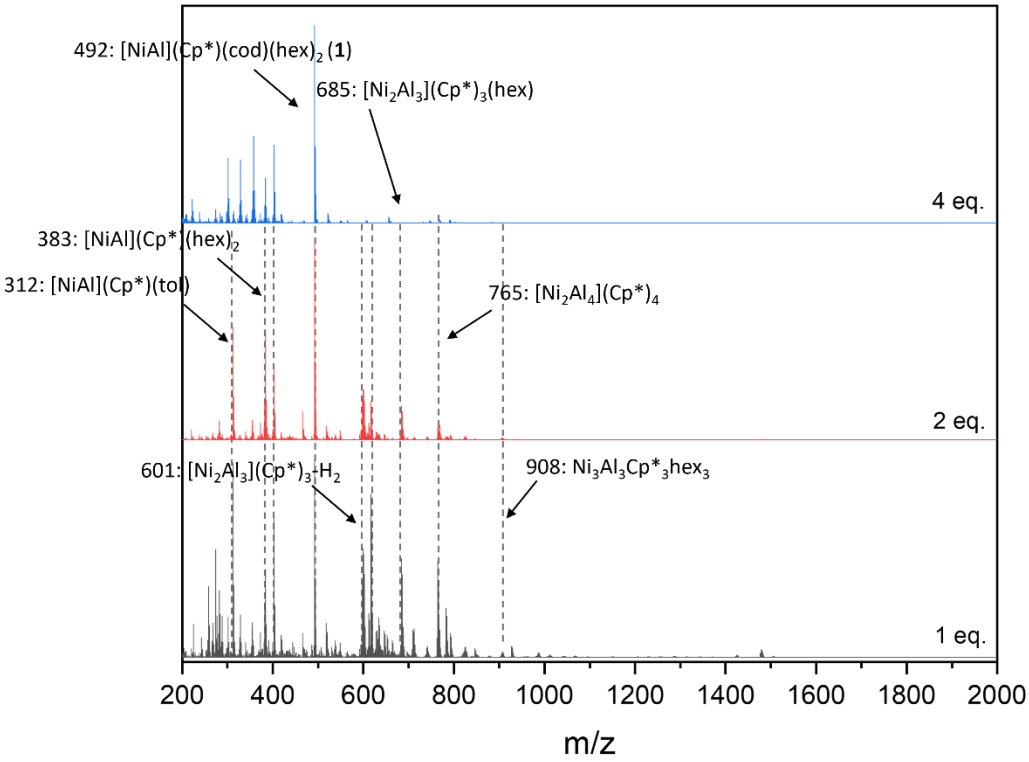



Fig. S 48. LIFDI mass spectra of the reaction $[Ni(cod)_2]$ (1eq.), AlCp* (1eq.) and hexyne (Δeq.) after 6 h at 60 °C in toluene/hexane. The formulas of the assigned signals only refers to

### Influence of additive amount at 90 °C

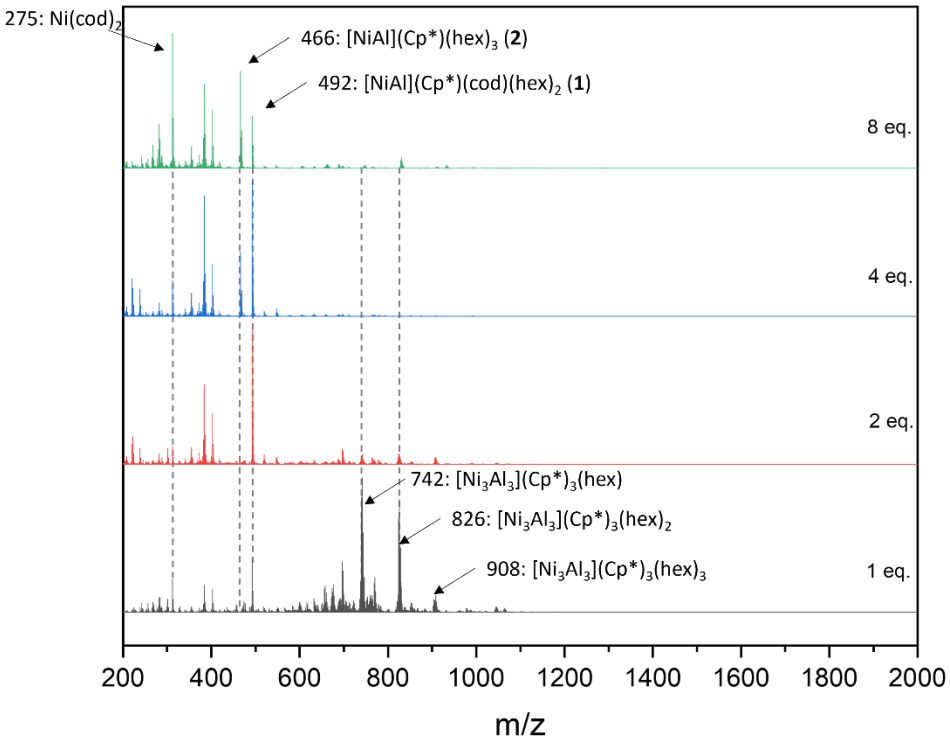



Fig. S 49. LIFDI mass spectra of the reaction $[Ni(cod)_2]$ (1eq.), AlCp* (1eq.) and hexyne (Δeq.) after 6.5 h at 90 °C in toluene/hexane.

## Influences on Ni/Ga cluster formation

### Influence of temperature on Ni/Ga cluster formation

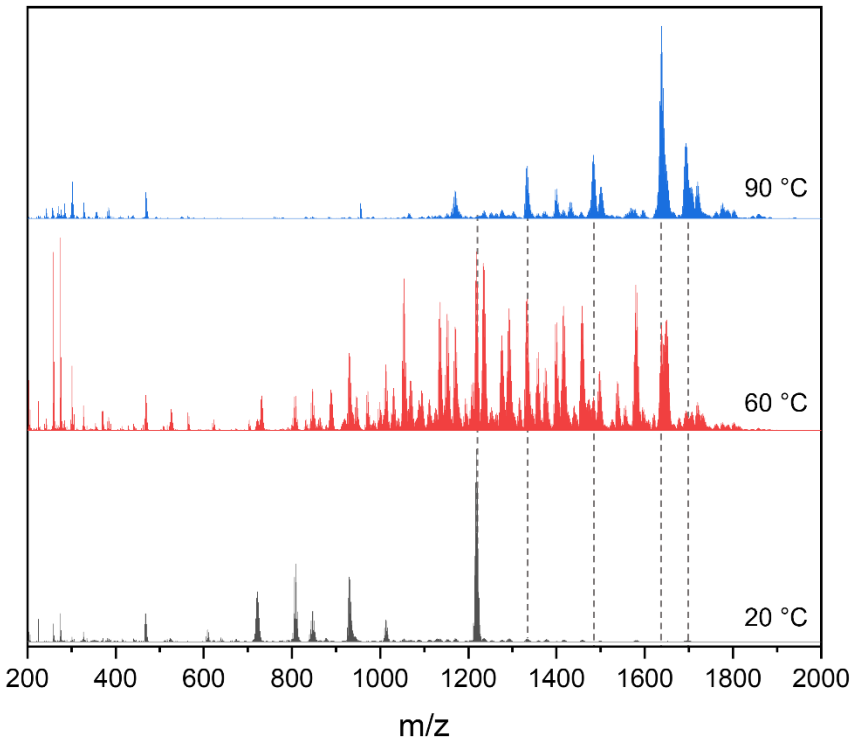



Fig. S 50. LIFDI mass spectra of the reaction of $[Ni(cod)_2]$ (1eq.), GaCp* (1eq.) and 3-hexyne (0.5eq.) at different temperatures showing a temperature dependent reaction behavior with the broadest product variety at 60 °C. Assignment of the spectra at 60 °C and 90 °C are given below. The room temperature spectra shows **3** (1218 m/z) as the favored product while the spectra at 90 °C reveal $[Ni_7Ga_6](Cp^*)_6$ (1637 m/z) and $[Ni_8Ga_6](Cp^*)_6$ (1695 m/z) as the major product.

## Signal Assignment of the reaction at 60 °C

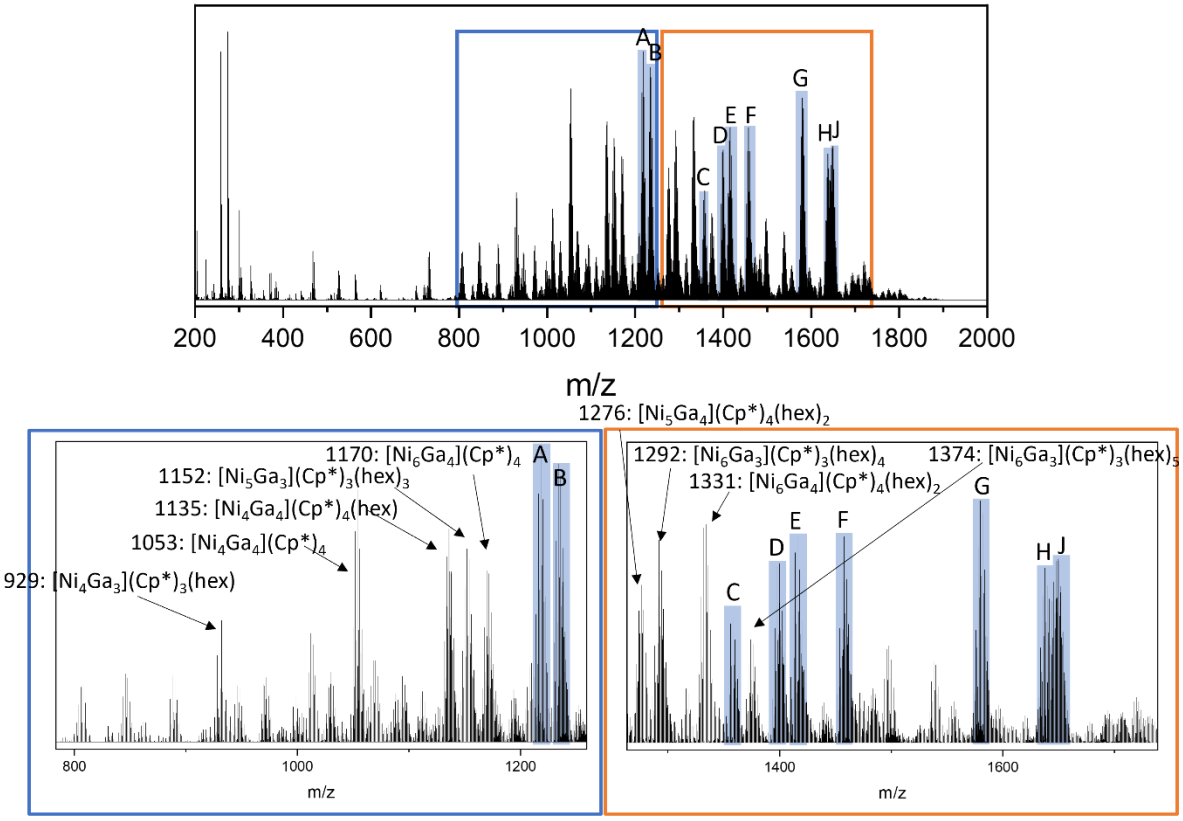



Fig. S 51. LIFDI mass distribution of the reaction of $[Ni(cod)_2]$ (1eq.) with 3-hexyne (0.5eq.) and GaCp* (1eq.) with a ratio 1: 0.5: 1 at 60 °C. Blue highlighted peaks are assigned as product while the others are related to instrument caused fragments.

Table S 2. Signal assignment of the reaction of $[Ni(cod)_2]$ with 3-hexyne and GaCp* with a ratio 1: 0.5: 1 at 60 °C.

| Experimental | Calculated | Cluster | Fragment |
|---|---|---|---|
| 929.9407 | 929.9432 | $[Ni_4Ga_3](Cp^*)_3(hex)$ | A-Cp*-hex |
| 1053.9047 | 1053.9065 | $[Ni_4Ga_4](Cp^*)_4$ | A-2hex |
| 1135.9836 | 1135.9842 | $[Ni_4Ga_4](Cp^*)_4(hex)$ | A-hex |
| 1152.0215 | 1152.0344 | $[Ni_5Ga_3](Cp^*)_3(hex)_3$ | B-GaCp* |
| 1169.7737 | 1169.7759 | $[Ni_6Ga_4](Cp^*)_4$ | E-3hex/G-2GaCp* |
| **1218.0633** | **1218.0633** | **$[Ni_4Ga_4](Cp^*)_4(hex)_2$** | **A** |
| **1234.0947** | **1234.1131** | **$[Ni_5Ga_3](Cp^*)_3(hex)_4$** | **B** |
| **1275.9908** | 1275.9973 | $[Ni_5Ga_4](Cp^*)_4(hex)_2$ | C-hex |
| **1292.0254** | 1292.0485 | $[Ni_6Ga_3](Cp^*)_3(hex)_4$ | 1374-hex |
| **1331.9120** | 1331.9350 | $[Ni_6Ga_4](Cp^*)_4(hex)_2$ | E-hex |
| **1358.0694** | **1358.0772** | **$[Ni_5Ga_4](Cp^*)_4(hex)_3$** | **C** |
| **1374.1051** | 1374.1268 | $[Ni_6Ga_3](Cp^*)_3(hex)_5$ | |
| **1399.9626** | **1399.9613** | **$[Ni_5Ga_5](Cp^*)_5(hex)$** | **D** |
| **1415.9936** | **1415.9933** | **$[Ni_6Ga_4](Cp^*)_4(hex)_3$-2H** | **E** |
| **1457.8911** | **1457.8958** | **$[Ni_6Ga_5](Cp^*)_5(hex)$** | **F** |
| **1579.8553** | **1579.8608** | **$[Ni_6Ga_6](Cp^*)_6$** | **G** |
| **1637.7793** | **1637.7943** | **$[Ni_7Ga_6](Cp^*)_6$** | **H** |
| **1649.7730** | **1649.7960** | **$[Ni_6Ga_7](Cp^*)_6$+H** | **J** |

*Note: The signal at 1374 m/z is an overlap of three different isotopic pattern, where $[Ni_6Ga_3](Cp^*)_3(hex)_5$ is the highest.*

## Influence of additive addition on Ni/Ga cluster formation

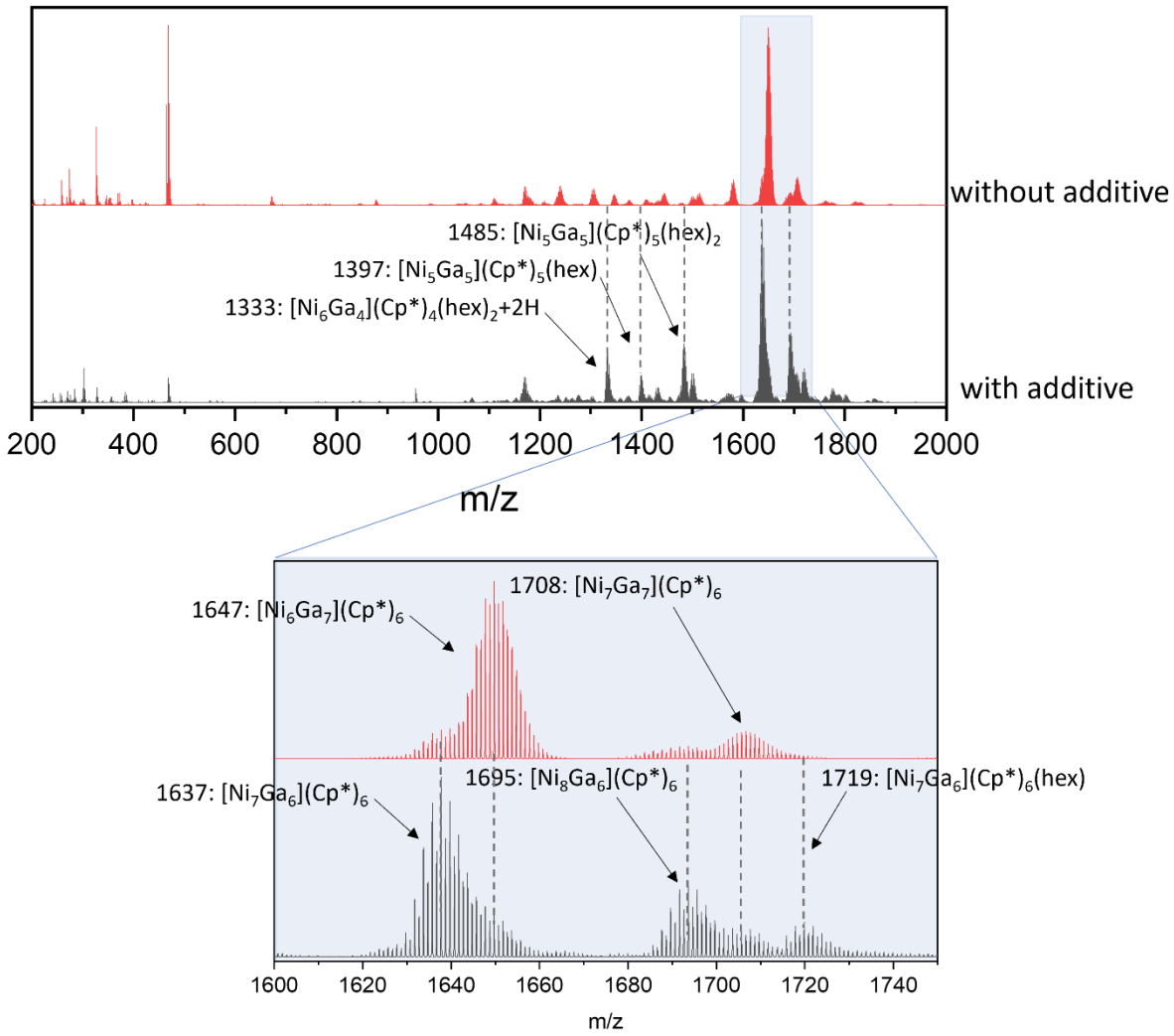



Fig. S 52. LIFDI mass spectra of the reaction $[Ni(cod)_2]$ (1eq.) and GaCp* (1eq.) at 90 °C after 6h showing the influence of the additive on cluster formation. Black: with additive (3-hexyne, 1eq.), red: without additive. Usage of additive led to the Ni-rich cluster $[Ni_7Ga_6](Cp^*)_6$ (1637 m/z), $[Ni_8Ga_6](Cp^*)_6$ (1695 m/z) and $[Ni_7Ga_6](Cp^*)_6(hex)$ (1719 m/z) as the major product while additive-free reaction favors Ga-enriched clusters as $[Ni_6Ga_7](Cp^*)_6$ (1647 m/z) and $[Ni_7Ga_7](Cp^*)_6$ (1708 m/z).

## Influence of additive amount on Ni/Ga cluster formation at 20 °C

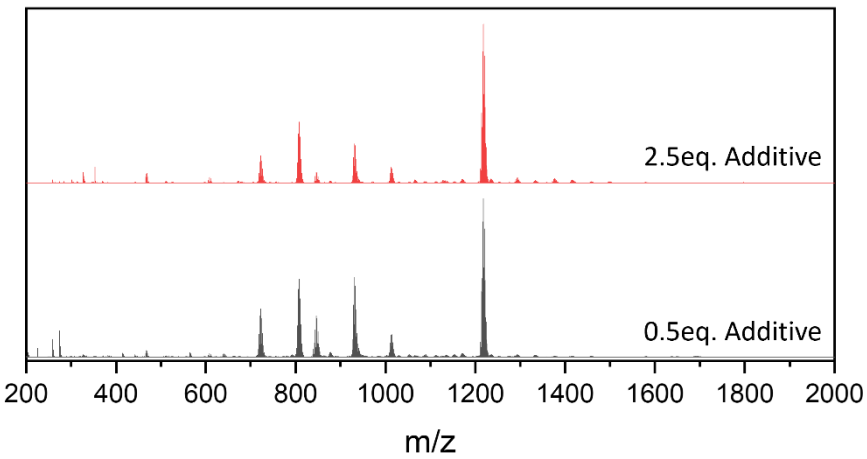



Fig. S 53. Studies on the influence of the additive amount on the reaction of $[Ni(cod)_2]$ (1eq.) with GaCp* (1eq.) at room temperature showing **3** (1218 m/z) as the major product regardless of the additive amount. LIFDI mass spectra were recorded after 1d.

**Influence of additive amount on Ni/Ga cluster formation at 60 °C**

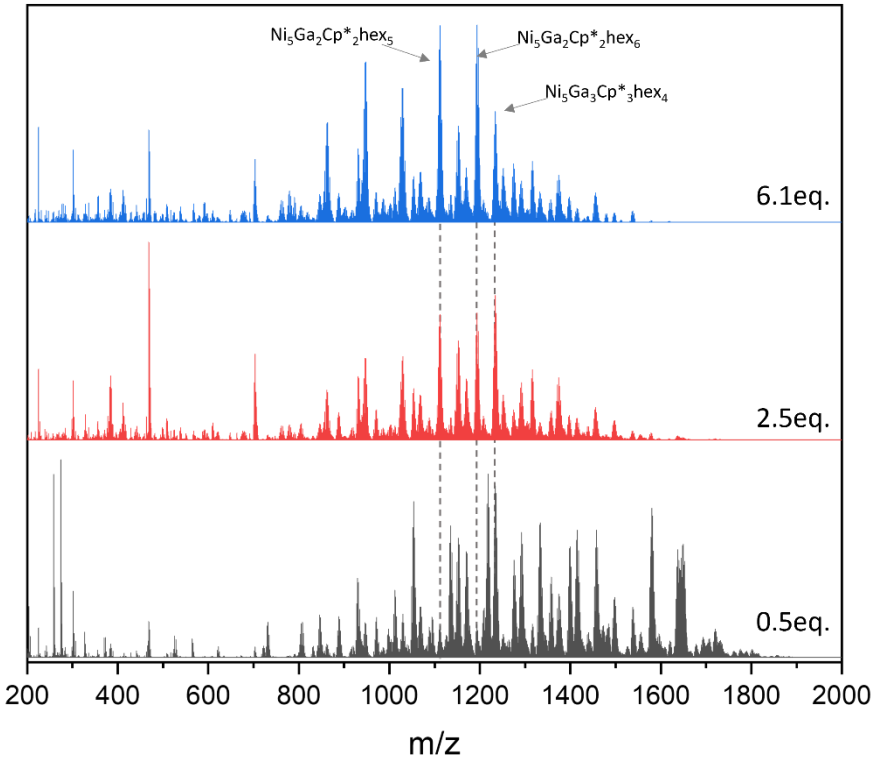



Fig. S 54. Studies on the influence of the additive amount on the reaction of $[Ni(cod)_2]$ (1eq.) with GaCp* (1eq.) at 60 °C showing a diverse reactivity. LIFDI mass spectra were recorded after 4.5 h. The more additive is used, the smaller are the obtained clusters but with increasing Ni-hex ratio.

## Additional MS data of the synthesis and analysis of 3

**Mass spectrum without fragmentation of 3**

As the ions pass the HCD cell of the MS instrument, the MS spectra are affected by fragmentation revealing the loss of GaCp* as well as hexyne. To make sure that this is only caused by instrument setup, we also recorded a mass spectrum of **3** at a JEOL AccuTOF GCx instrument equipped with a LIFDI ion source at the University of Heidelberg. Although the measurement confirms our assumption of fragmentation, the resolution on this device was much lower.

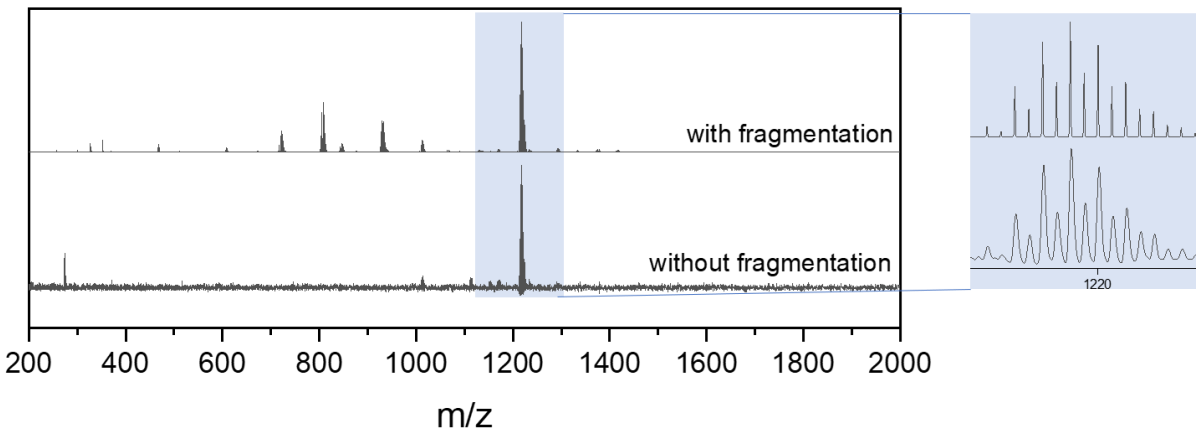



Fig. S 55. Comparison of LIFDI mass distribution of **3** measured on either an Exactive Orbitrap System (Thermo Fischer, top) revealing fragmentation or a JEOL AccuTOF instrument where no fragmentation was observed.

## Fragmentation experiments of 3

Moreover, we validated the MS results by gradual increase of the RF voltage of the HCD from 10.0 up to 40.0. Signals that are increasing during all spectra are assigned as fragments while only decreasing signals are named as the product. If one signal is increasing and decreasing related to an intermediate which is built during fragmentation process. This allowed us to define 1218 m/z as product, while the other signals can only be assigned to intermediates or fragments.

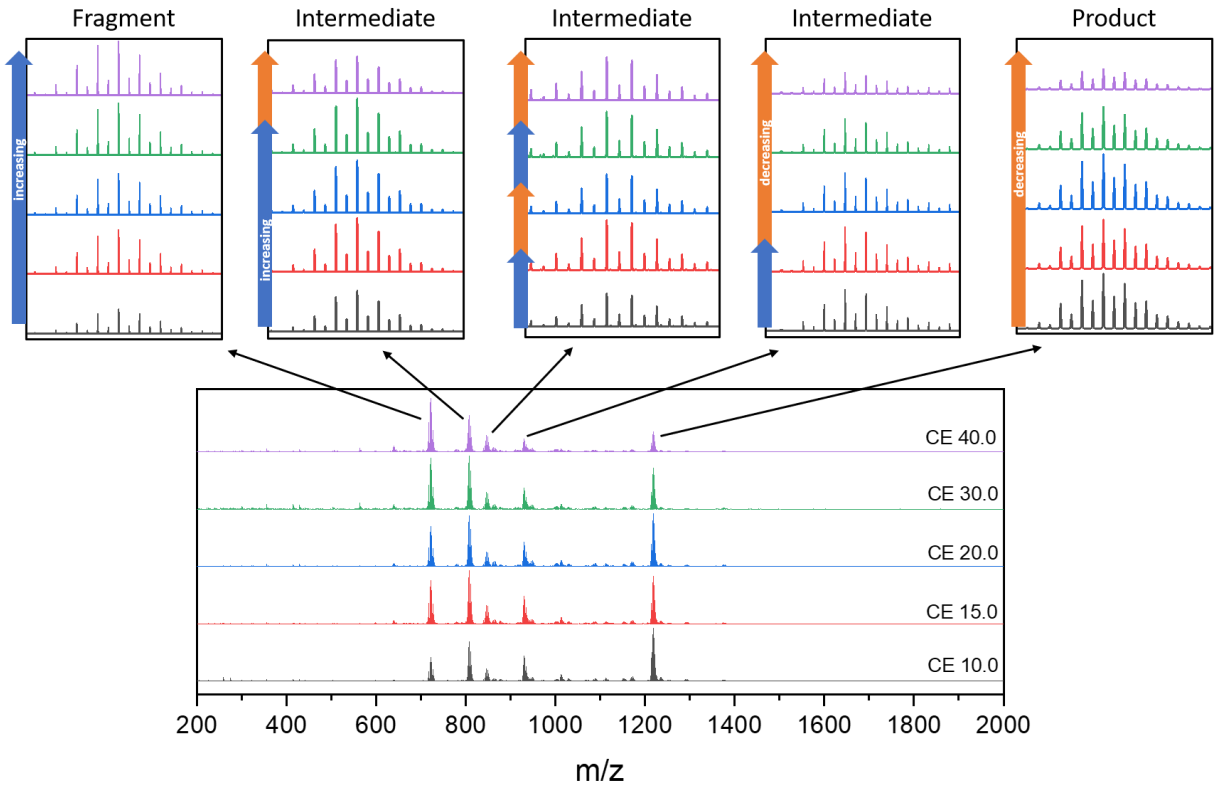



Fig. S 56. LIFDI mass distributions of $[Ni_4Ga_4](Cp^*)_4(hex)_2$ (**3**) at different RF voltages of the HCD cell.

## Labelling experiment of 3

Furthermore, we performed labelling experiments with $GaCp^{*Et}$ instead of GaCp* where one methyl group is exchanged by an ethyl group to support our assumption of the sum formula.

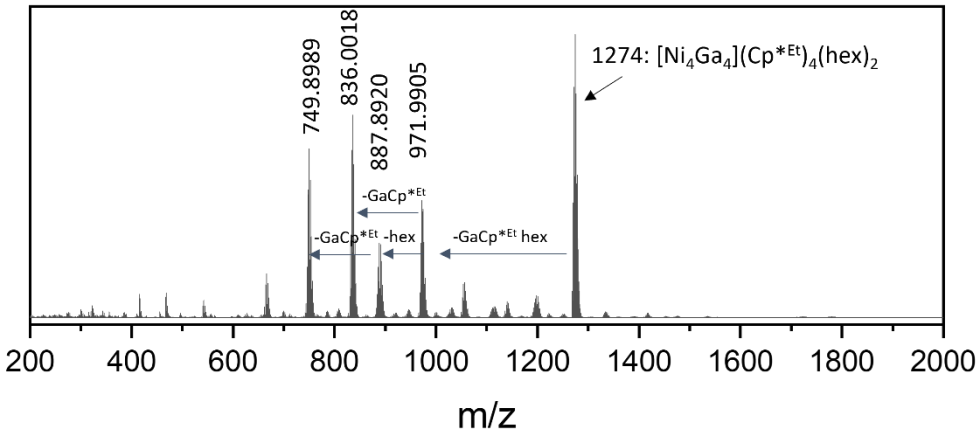



Fig. S 57. LIFDI mass distribution of the reaction $[Ni(cod)_2]$ (1eq.), $GaCp^{*Et}$ (1eq.) and hexyne (1eq.) after 2 h at room temperature in toluene showing $[Ni_4Ga_4](Cp^{*Et})_4(hex)_2$ (found: 1274.1253, calcd: 1274.1264).

## In-situ monitoring of the synthesis of 3

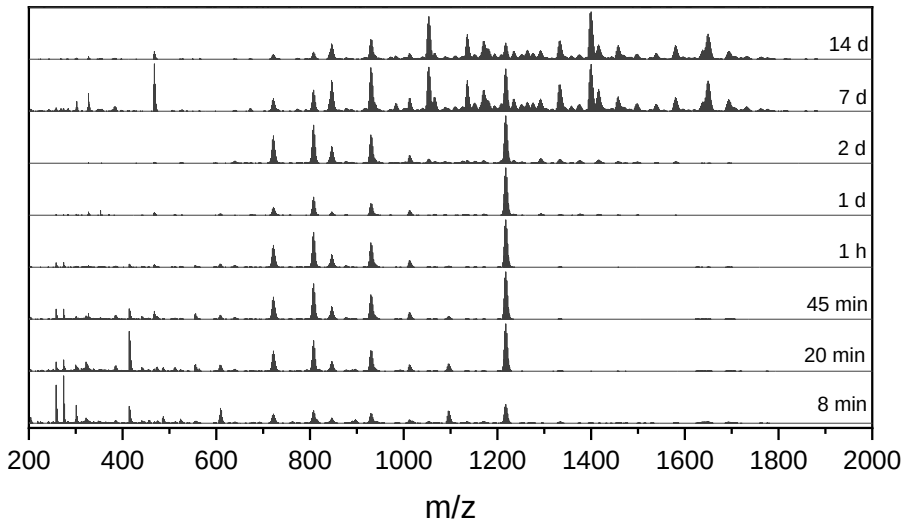



Fig. S 58. *In-situ* LIFDI MS measurements to monitor the synthesis of **3**.

*In-situ* LIFDI MS measurements were used to monitor the synthesis of **3**. After one day in solution the formation of bigger clusters as $[Ni_8Ga_6](Cp^*)_6$ (1695 m/z), $[Ni_6Ga_7](Cp^*)_6$ (1647 m/z), $[Ni_7Ga_6](Cp^*)_6$ (1637 m/z), $[Ni_6Ga_6](Cp^*)_6$ (1577 m/z), $[Ni_6Ga_5](Cp^*)_5(hex)_1$ (1456 m/z), $[Ni_6Ga_4](Cp^*)_4(hex)_3$ (1414 m/z), $[Ni_5Ga_5](Cp^*)_5(hex)_1$ (1398 m/z) and $[Ni_6Ga_4](Cp^*)_4(hex)_2$ (1332 m/z) were obtained.

## Reactivity tests of 3

*Procedure details:* **3** was synthesized as described above. Afterwards the influence and reactivity of GaCp* on **3** was investigated by stepwise addition of several equivalents GaCp* with a reaction time of min. 3 h each at room temperature. The progress and influence were monitored using *in-situ* LIFDI mass spectrometry. As it can be seen in Fig. S 59, **3** (m/z = 1218) is stable for several hours without further reaction with GaCp*, only the formation of $[NiGa_2]Cp^*_2$ at 468 m/z and fragments of **3** could be detected to increase.

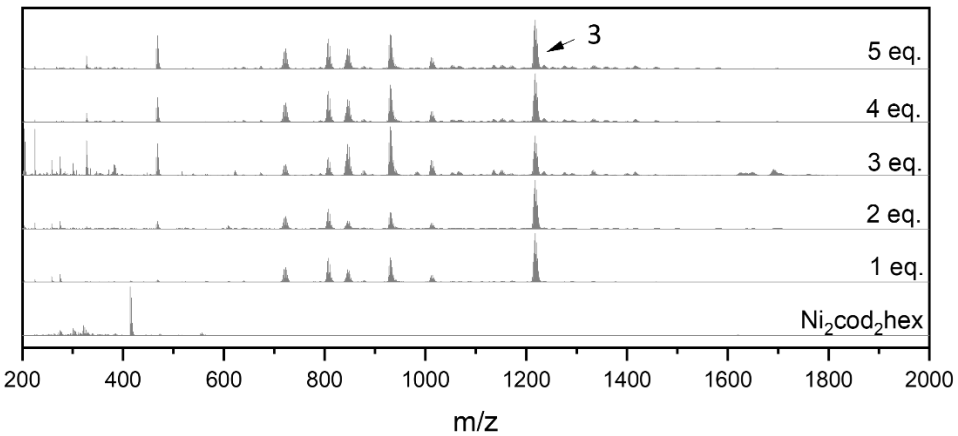



Fig. S 59. *In-situ* LIFDI mass spectra of the stepwise addition of GaCp* (regarding to nickel) to a mixture of $[Ni(cod)_2]$ (1eq.) and hexyne (0.5eq.) to investigate the influence on the product formation at room temperature. The spectra show an increase of the signal at 468 m/z referring to overlapped signals $[NiGa_2](Cp^*)_2$ and $[Ni_2](Cp^*)_2(hex)$.

## Reaction of Ni/Al and Ni/Ga clusters with hydrogen

In the following, we are investigating the influence of a $H_2$ as fourth component in the system on the cluster growth processes. Reaction of $[Ni_4Ga_4](Cp^*)_4(hex)_2$ (**3**) under $H_2$ pressure either lead to hydrogenated clusters **3+H$_m$** (m = 2 to 6), or initiate cluster growth reactions resulting in the formation of $[Ni_5Ga_5](Cp^*)_5(hex)_n(H)_{2m}$ (m = 1, 2) while releasing hydrogenated organic products. Our working hypothesis is the $[Ni_5Ga_5]$ cluster bearing hexene instead of hexyne which is supported by means of NMR spectroscopy. Also larger clusters such as $[Ni_6Ga_7](Cp^*)_6$ show the potential to bind hydrogen on the cluster shell or core, respectively. Treatment of **1** with $H_2$ lead to cleavage of full hydrogenation of all unsaturated ligands (cod or hexyne dimer), whereas **2** show stepwise hydrogenation of the *side-on* coordinated hexyne determined by *cis*-hexene and afterwards hexane.

### Reaction of 1 with $H_2$

*Procedure A: **1** was synthesized as described above. **1** (10.2 mg, 0.021 mmol, 1.0eq.) was dissolved in 0.34 mL toluene-d$_8$ and subsequently, 3-hexyne (0.16 mL as 1 M solution in tol-d$_8$, 0.16 mmol, 7.7 eq.) was added and pressurized with 1 bar $H_2$ at room temperature. The NMR spectra were recorded* in-situ.

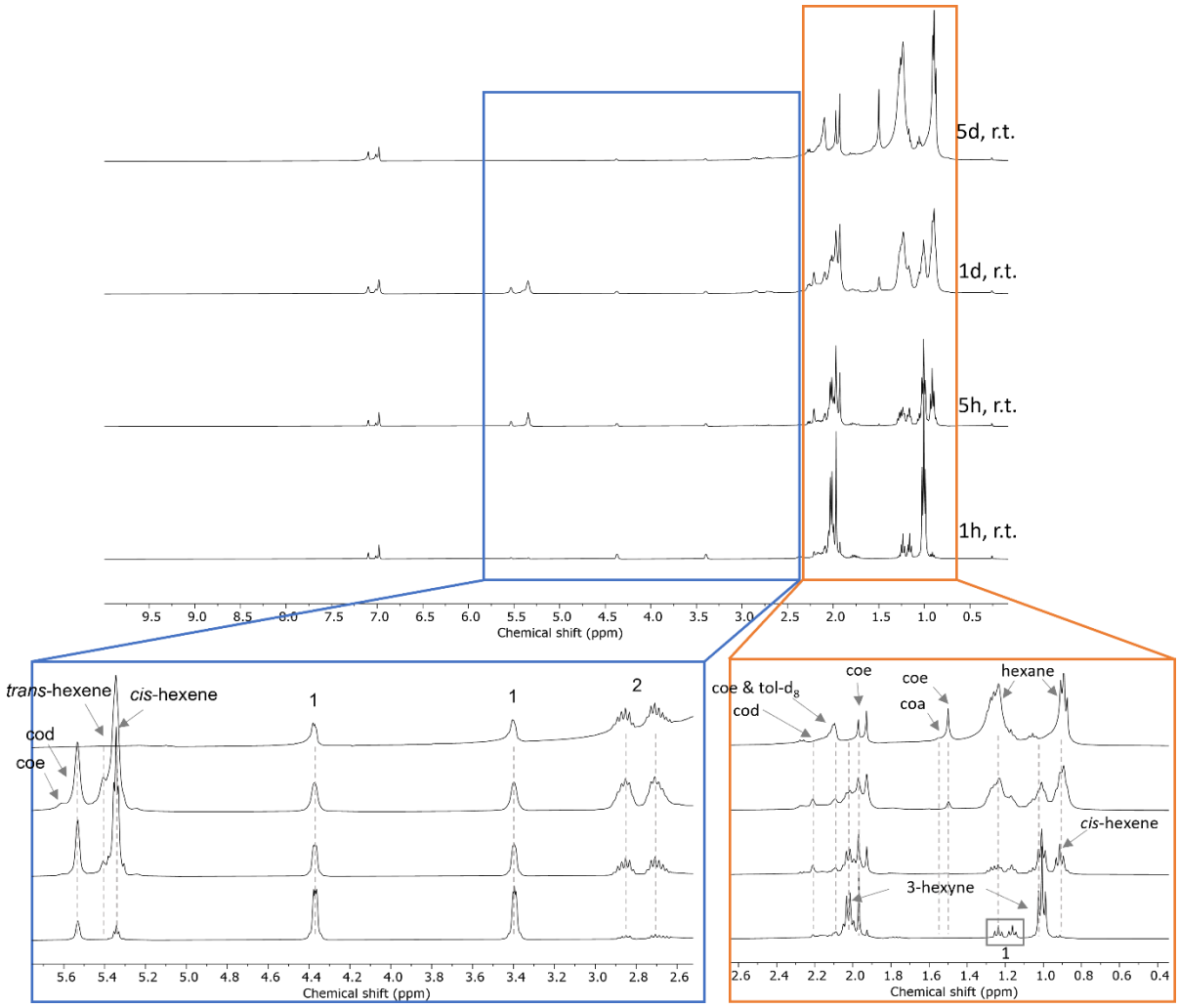



Fig. S 60. Time-dependent $^1$H NMR spectra of the reaction of **1** with $H_2$ and excess 3-hexyne at r.t.. Abbreviations: cod: 1,5-cyclooctadiene; coe: cyclooctene; coa: cyclooctane, tol-d$_8$: deuterated toluene.

The NMR spectra reveals the conversion of **1**, 3-hexyne and COD resulting in the formation of **2** and the respective alkene (*cis*-hexene/*trans*-hexene, cyclooctene) and alkane (hexane, cyclooctane) species catalyzed by a Ni/Al cluster.

**Reaction of 2 with $H_2$**

*Procedure A: **2** (0.009 mmol) was synthesized following the procedure above. For the reactivity tests, the reaction was performed in toluene-$d_8$ and cooling to room temperature, the mixture was pressurized with 1 bar $H_2$ at room temperature. It has to be noted that the mixture still contains **1** and hexyne in excess. The NMR spectra were recorded* in-situ.

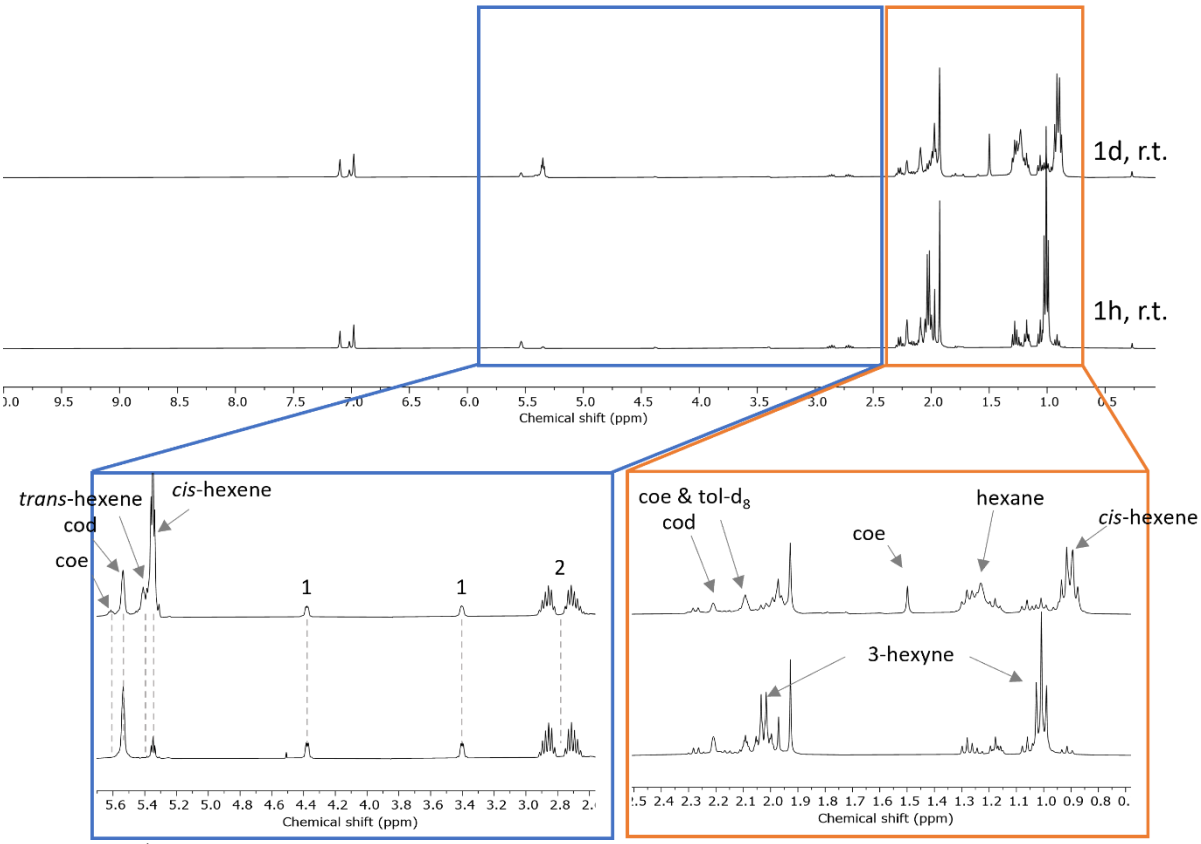



Fig. S 61. Time-dependent $^1$H NMR spectra of the reaction of **2** with $H_2$ and excess 3-hexyne at r.t.. Abbreviations: cod: 1,5-cyclooctadiene; coe: cyclooctene; tol-$d_8$: deuterated toluene.

The NMR spectra reveals the conversion of 3-hexyne and COD resulting in formation of the respective alkene (cis-hexene/trans-hexene, cyclooctene) and alkane (hexane, cyclooctane) species catalyzed by a Ni/Al cluster. In contrast to **1**, **2** only undergoes the semihydrogenation preferring the *cis*-alkene and only small amounts of hexene is fully hydrogenated to hexane.

**Reaction of 3 with $H_2$ under different conditions**

*Procedure: **3** (0.20 mmol) was synthesized as described above. After stirring for 3.5 h at room temperature, the mixture was shortly exposed to vacuo to remove residual cod or hexyne. The residue was resolved in 2 mL toluene-$d_8$ and divided into four equal parts (0.05 mmol).*

*A: Reference*

*B: Addition of 1 bar $H_2$*

*C: Addition of 1 bar $H_2$ and 3-hexyne (excess)*

*D: Addition of 1 bar $H_2$ and $C_6H_{12}$ as internal standard*

The NMR spectra reveals the conversion of hexyne and COD resulting in the respective alkene and alkane species catalyzed by a Ni/Ga cluster.

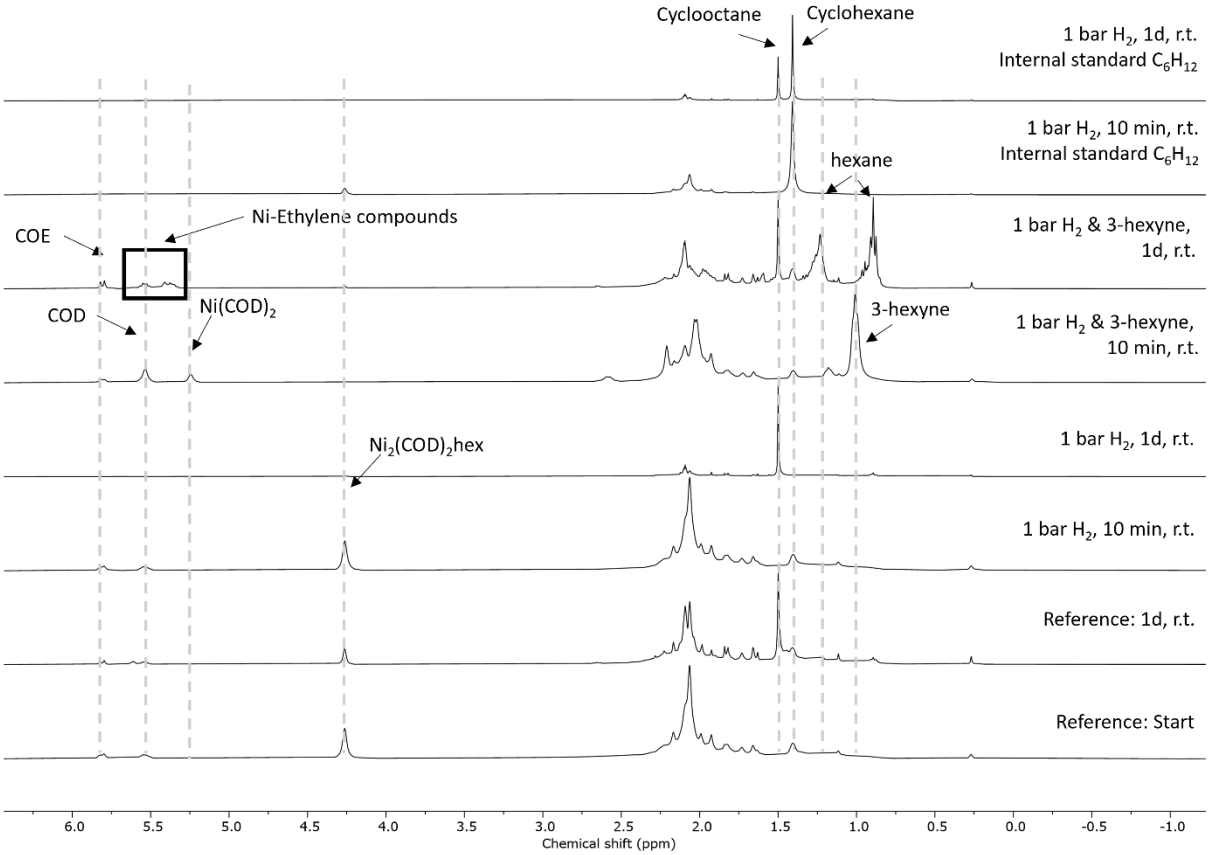



Fig. S 62. Time-dependent $^1$H NMR spectra of the reaction of **3** with hydrogen in toluene-$d_8$. Abbreviations: COD: 1,5-cyclooctadiene, COE: cyclooctene.

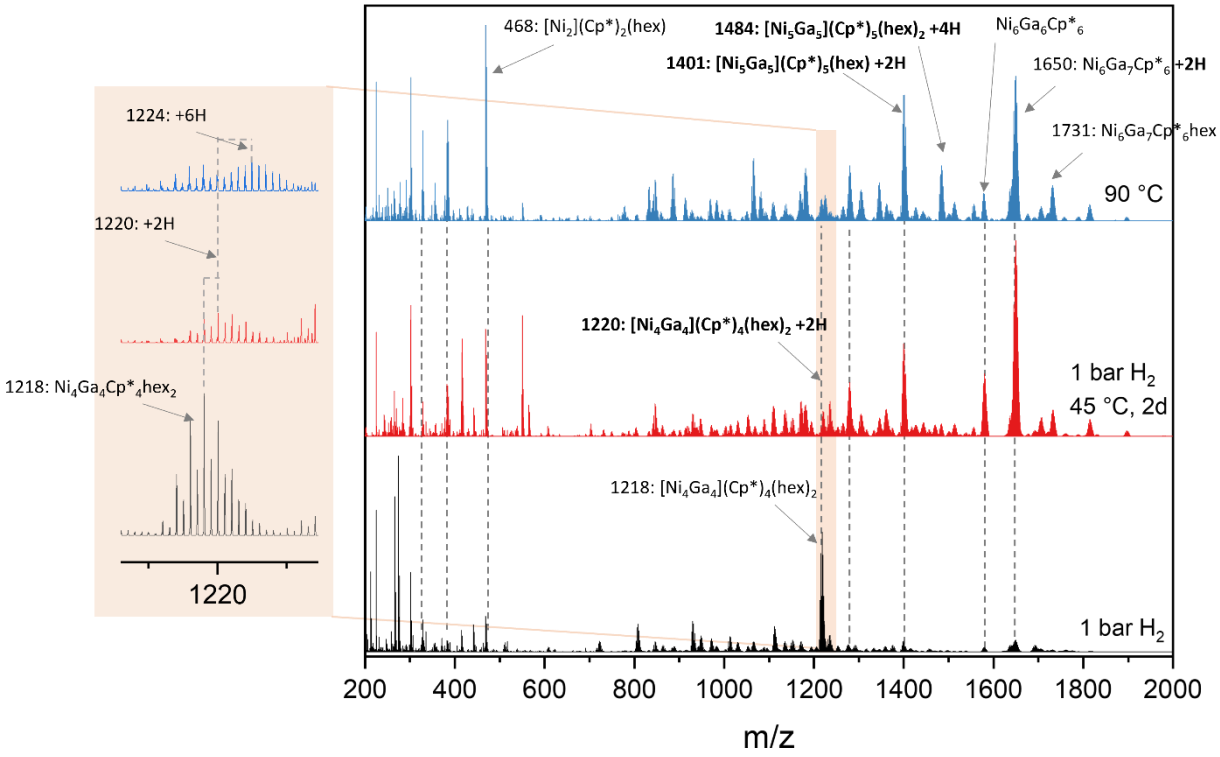
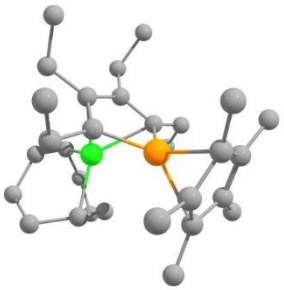



Fig. S 63: LIFDI mass spectrum of **3** with hydrogen in toluene-$d_8$.

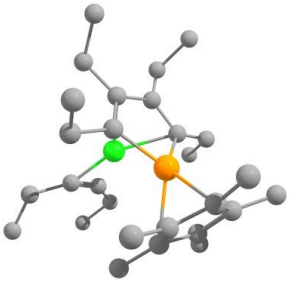
**Theoretical Results – XYZ coordinates of calculated molecules**

## Optimized geometries on the BP86-D3/def2-tzvpp level of theory

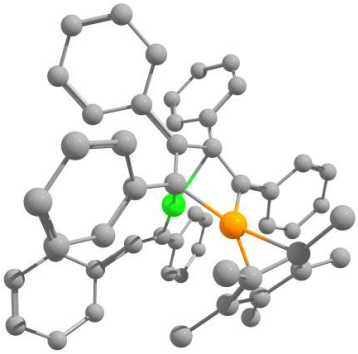
*Color code: C, grey; H, white; Al, orange; Ga, blue; Ni, green.*



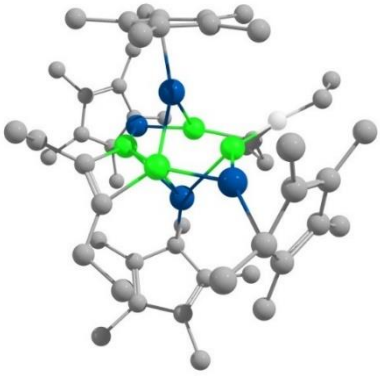
[NiAl](Cp*)(tebd)(cod)



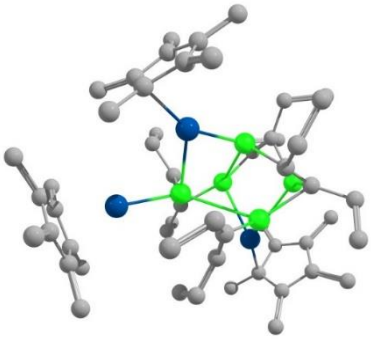
[NiAl](Cp*)(tebd)(hex)



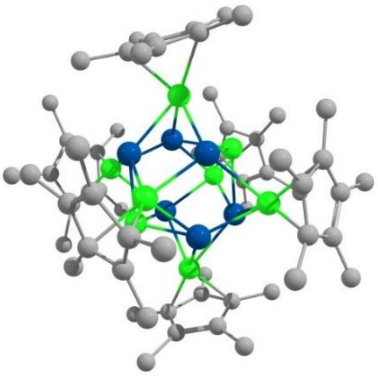
[NiAl](Cp*)(tpbd)(dpa)



$[Ni_4Ga_4](Cp^*)_4(hex)_2$



$[Ni_5Ga_3](Cp^*)_3(hex)_4$



$[Ni_8Ga_6](Cp^*)_6$

## Coordinates of BP86/TZVPP optimized molecules

**[NiAl](Cp*)(tebd)(cod)**

| | | | |
|---|---|---|---|
| Ni | 10.259551000 | 5.588918000 | 7.836298000 |
| Al | 9.218503000 | 3.153823000 | 7.909292000 |
| C | 11.888388000 | 4.794366000 | 6.887963000 |
| H | 11.666088000 | 3.772042000 | 6.541004000 |
| C | 12.168310000 | 4.955049000 | 8.264107000 |
| H | 12.102432000 | 4.044106000 | 8.882942000 |
| C | 13.015318000 | 6.084856000 | 8.844629000 |
| H | 13.803996000 | 6.360110000 | 8.113022000 |
| H | 13.558020000 | 5.709274000 | 9.736465000 |
| C | 12.183911000 | 7.332524000 | 9.237869000 |
| H | 11.906000000 | 7.259056000 | 10.307512000 |
| H | 12.808026000 | 8.254460000 | 9.152274000 |
| C | 10.905916000 | 7.475012000 | 8.430635000 |
| H | 10.073171000 | 7.979291000 | 8.949757000 |
| C | 10.852892000 | 7.419820000 | 7.026352000 |
| H | 9.970106000 | 7.855493000 | 6.533443000 |
| C | 12.079385000 | 7.229266000 | 6.144438000 |
| H | 11.964836000 | 7.822925000 | 5.214237000 |
| H | 12.976672000 | 7.638838000 | 6.652912000 |
| C | 12.298110000 | 5.743454000 | 5.779393000 |
| H | 11.684930000 | 5.496652000 | 4.887982000 |
| H | 13.357897000 | 5.561305000 | 5.477405000 |
| C | 8.688223000 | 1.166209000 | 9.022124000 |
| C | 8.289433000 | 1.101019000 | 7.636188000 |
| C | 9.472946000 | 1.190091000 | 6.825957000 |
| C | 10.596748000 | 1.380510000 | 7.710135000 |
| C | 10.105537000 | 1.335695000 | 9.069229000 |
| C | 7.733844000 | 1.134455000 | 10.181469000 |
| H | 7.107780000 | 2.051797000 | 10.229502000 |
| H | 8.269734000 | 1.055689000 | 11.146837000 |
| H | 7.044067000 | 0.268067000 | 10.110456000 |
| C | 6.880404000 | 0.923383000 | 7.144252000 |
| H | 6.153851000 | 1.487504000 | 7.763183000 |
| H | 6.571991000 | -0.144644000 | 7.167188000 |
| H | 6.766875000 | 1.275409000 | 6.100068000 |
| C | 9.547415000 | 1.032528000 | 5.336367000 |
| H | 8.637477000 | 1.410400000 | 4.832552000 |
| H | 9.655582000 | -0.038645000 | 5.057960000 |
| H | 10.414100000 | 1.570741000 | 4.905283000 |
| C | 12.049161000 | 1.336755000 | 7.322650000 |
| H | 12.205441000 | 1.616022000 | 6.262753000 |
| H | 12.454301000 | 0.308742000 | 7.451303000 |
| H | 12.671705000 | 2.013831000 | 7.939238000 |
| C | 10.986674000 | 1.430275000 | 10.281522000 |
| H | 11.769592000 | 0.642420000 | 10.267252000 |
| H | 10.409206000 | 1.308169000 | 11.217508000 |
| H | 11.512691000 | 2.406401000 | 10.347678000 |
| C | 7.684605000 | 4.046973000 | 4.337499000 |
| H | 6.858111000 | 4.776367000 | 4.449999000 |
| H | 7.323302000 | 3.087306000 | 4.761424000 |
| H | 7.859167000 | 3.898644000 | 3.251377000 |
| C | 8.956526000 | 4.522570000 | 5.059825000 |
| H | 9.795684000 | 3.852592000 | 4.775056000 |
| H | 9.238618000 | 5.525821000 | 4.661596000 |
| C | 8.834122000 | 4.543090000 | 6.566200000 |
| C | 8.267936000 | 5.647172000 | 7.257718000 |
| C | 8.350629000 | 5.606446000 | 8.749020000 |
| C | 8.982930000 | 4.482996000 | 9.332614000 |
| C | 9.164848000 | 4.369266000 | 10.834382000 |
| H | 8.249025000 | 4.721934000 | 11.359839000 |
| H | 9.251522000 | 3.299272000 | 11.110372000 |
| C | 10.373396000 | 5.109367000 | 11.426077000 |
| H | 11.318516000 | 4.752319000 | 10.971854000 |
| H | 10.441075000 | 4.961051000 | 12.524470000 |
| H | 10.313641000 | 6.198703000 | 11.232217000 |
| C | 7.601095000 | 6.809492000 | 6.545494000 |
| H | 8.017801000 | 6.882320000 | 5.520125000 |
| H | 7.856827000 | 7.770906000 | 7.038785000 |

| | | | |
|---|---|---|---|
| C | 6.070257000 | 6.688116000 | 6.454747000 |
| H | 5.643327000 | 7.495725000 | 5.825042000 |
| H | 5.594240000 | 6.755780000 | 7.452041000 |
| H | 5.770999000 | 5.716005000 | 6.014398000 |
| C | 7.709050000 | 6.693822000 | 9.593591000 |
| H | 7.613588000 | 7.635812000 | 9.017048000 |
| H | 8.369697000 | 6.934367000 | 10.451479000 |
| C | 6.324762000 | 6.281894000 | 10.128601000 |
| H | 5.629967000 | 6.028692000 | 9.303681000 |
| H | 5.864656000 | 7.097587000 | 10.723658000 |
| H | 6.393969000 | 5.385889000 | 10.777258000 |

**[NiAl](Cp*)(tebd)(hex)**

| | | | |
|---|---|---|---|
| Ni | 9.843280000 | 5.399914000 | 8.128248000 |
| Al | 8.850919000 | 3.135884000 | 7.997255000 |
| C | 8.887312000 | 1.083572000 | 8.966566000 |
| C | 8.408609000 | 0.961580000 | 7.614178000 |
| C | 9.474213000 | 1.333203000 | 6.732078000 |
| C | 10.577967000 | 1.763102000 | 7.530431000 |
| C | 10.218621000 | 1.588109000 | 8.915694000 |
| C | 8.097210000 | 0.715815000 | 10.185727000 |
| H | 7.143918000 | 1.261048000 | 10.246480000 |
| H | 8.656782000 | 0.927734000 | 11.104371000 |
| H | 7.858896000 | -0.358706000 | 10.186221000 |
| C | 7.073751000 | 0.415890000 | 7.203573000 |
| H | 6.301453000 | 0.629405000 | 7.954139000 |
| H | 7.111252000 | -0.677799000 | 7.075109000 |
| H | 6.737594000 | 0.843944000 | 6.249750000 |
| C | 9.440665000 | 1.212529000 | 5.241387000 |
| H | 8.480421000 | 1.535562000 | 4.819711000 |
| H | 9.592058000 | 0.164305000 | 4.938111000 |
| H | 10.230249000 | 1.806011000 | 4.765288000 |
| C | 11.910241000 | 2.247236000 | 7.045826000 |
| H | 11.870445000 | 2.539945000 | 5.989187000 |
| H | 12.679647000 | 1.465916000 | 7.145254000 |
| H | 12.245318000 | 3.126390000 | 7.613437000 |
| C | 11.124530000 | 1.896259000 | 10.066842000 |
| H | 11.917178000 | 1.138178000 | 10.163401000 |
| H | 10.579338000 | 1.932420000 | 11.017113000 |
| H | 11.616673000 | 2.869494000 | 9.932485000 |
| C | 7.444676000 | 4.153194000 | 4.420433000 |
| H | 6.636001000 | 4.887213000 | 4.533899000 |
| H | 7.063387000 | 3.193294000 | 4.797703000 |
| H | 7.656614000 | 4.042425000 | 3.347298000 |
| C | 8.693334000 | 4.589816000 | 5.202016000 |
| H | 9.523801000 | 3.913448000 | 4.952731000 |
| H | 9.006218000 | 5.585607000 | 4.843642000 |
| C | 8.470924000 | 4.570691000 | 6.690971000 |
| C | 7.926655000 | 5.662087000 | 7.384286000 |
| C | 7.860679000 | 5.544942000 | 8.875178000 |
| C | 8.412001000 | 4.397799000 | 9.455502000 |
| C | 8.474941000 | 4.239458000 | 10.959771000 |
| H | 7.540527000 | 4.598463000 | 11.422209000 |
| H | 8.531454000 | 3.171512000 | 11.213322000 |
| C | 9.659492000 | 4.949461000 | 11.629022000 |
| H | 10.606900000 | 4.539282000 | 11.261713000 |
| H | 9.630165000 | 4.830794000 | 12.722465000 |
| H | 9.663394000 | 6.022429000 | 11.395244000 |
| C | 7.517739000 | 6.951212000 | 6.703002000 |
| H | 8.023434000 | 7.005137000 | 5.729577000 |
| H | 7.888883000 | 7.812656000 | 7.278593000 |
| C | 6.003579000 | 7.099404000 | 6.483390000 |
| H | 5.784514000 | 7.981992000 | 5.866240000 |
| H | 5.463678000 | 7.213988000 | 7.431224000 |
| H | 5.592595000 | 6.217572000 | 5.973906000 |
| C | 7.199100000 | 6.630816000 | 9.697755000 |
| H | 7.212696000 | 7.590569000 | 9.165155000 |
| H | 7.764654000 | 6.789513000 | 10.625809000 |
| C | 5.746738000 | 6.260601000 | 10.050130000 |
| H | 5.156708000 | 6.060715000 | 9.146362000 |
| H | 5.255809000 | 7.070974000 | 10.606937000 |
| H | 5.710296000 | 5.353026000 | 10.666746000 |

| | | | |
|---|---|---|---|
| C | 11.473204000 | 5.804875000 | 7.331351000 |
| C | 11.629687000 | 5.747411000 | 8.613884000 |
| C | 11.997492000 | 5.956958000 | 5.953906000 |
| C | 13.527248000 | 5.912725000 | 5.843585000 |
| H | 11.617591000 | 6.905256000 | 5.538976000 |
| H | 11.552999000 | 5.173549000 | 5.319512000 |
| H | 13.988435000 | 6.726210000 | 6.417581000 |
| H | 13.846158000 | 6.008398000 | 4.795992000 |
| H | 13.917957000 | 4.963373000 | 6.234194000 |
| C | 12.554036000 | 5.845129000 | 9.771584000 |
| C | 13.971800000 | 6.306546000 | 9.411918000 |
| H | 12.600461000 | 4.863519000 | 10.272509000 |
| H | 12.115162000 | 6.520054000 | 10.523300000 |
| H | 14.449747000 | 5.603424000 | 8.717656000 |
| H | 14.599486000 | 6.381077000 | 10.311274000 |
| H | 13.949673000 | 7.292441000 | 8.928342000 |

**[NiAl](Cp*)(tpbd)(dpa)**

| | | | |
|---|---|---|---|
| Ni | 6.394373000 | 3.066933000 | 6.319277000 |
| Al | 7.875532000 | 1.289400000 | 5.520790000 |
| C | 8.113182000 | 4.063450000 | 5.656085000 |
| C | 8.519305000 | 2.953013000 | 6.421980000 |
| C | 9.442385000 | 3.064116000 | 7.561132000 |
| C | 9.116467000 | 2.496877000 | 8.813741000 |
| C | 10.007785000 | 2.557540000 | 9.894524000 |
| C | 11.260655000 | 3.175444000 | 9.744111000 |
| C | 11.602957000 | 3.742115000 | 8.502200000 |
| C | 10.705587000 | 3.693561000 | 7.426963000 |
| C | 7.724025000 | -0.739969000 | 4.565844000 |
| C | 9.101056000 | -0.423200000 | 4.870553000 |
| C | 10.225813000 | -0.342000000 | 3.876646000 |
| C | 9.235179000 | -0.318309000 | 6.308243000 |
| C | 7.933665000 | -0.491538000 | 6.880764000 |
| C | 7.558930000 | -0.526689000 | 8.333963000 |
| C | 6.994048000 | -0.742648000 | 5.800964000 |
| C | 5.538446000 | -1.043240000 | 6.018721000 |
| C | 10.525807000 | -0.066482000 | 7.031589000 |
| C | 7.194314000 | -1.019307000 | 3.190362000 |
| C | 6.807350000 | 2.466206000 | 4.291827000 |
| C | 5.858010000 | 2.019685000 | 3.260382000 |
| C | 6.117709000 | 2.212027000 | 1.880278000 |
| C | 5.252650000 | 1.703037000 | 0.900984000 |
| C | 4.098981000 | 0.989347000 | 1.270362000 |
| C | 3.830020000 | 0.782521000 | 2.633661000 |
| C | 4.702674000 | 1.281806000 | 3.609932000 |
| C | 7.170727000 | 3.807198000 | 4.520887000 |
| C | 6.535514000 | 4.983489000 | 3.853123000 |
| C | 6.842010000 | 5.355239000 | 2.529559000 |
| C | 6.228768000 | 6.472910000 | 1.940932000 |
| C | 5.303867000 | 7.237420000 | 2.670226000 |
| C | 5.002931000 | 6.883985000 | 3.996880000 |
| C | 5.617914000 | 5.769310000 | 4.583076000 |
| C | 8.499396000 | 5.464986000 | 5.978217000 |
| C | 8.273262000 | 5.993332000 | 7.265620000 |
| C | 8.651013000 | 7.305812000 | 7.577703000 |
| C | 9.269225000 | 8.110735000 | 6.605126000 |
| C | 9.503514000 | 7.592706000 | 5.320319000 |
| C | 9.117655000 | 6.280653000 | 5.007747000 |
| C | 5.415385000 | 2.875119000 | 7.907299000 |
| C | 5.560037000 | 2.738796000 | 9.339503000 |
| C | 4.882390000 | 1.699398000 | 10.030288000 |
| C | 5.054664000 | 1.526138000 | 11.409637000 |
| C | 5.894277000 | 2.392388000 | 12.133432000 |
| C | 6.562030000 | 3.432920000 | 11.464326000 |
| C | 6.404610000 | 3.599634000 | 10.082670000 |
| C | 4.626645000 | 2.831314000 | 6.860375000 |
| C | 3.287604000 | 2.729748000 | 6.326071000 |
| C | 2.964755000 | 3.329939000 | 5.083073000 |
| C | 1.669784000 | 3.230515000 | 4.559895000 |
| C | 0.677061000 | 2.520492000 | 5.257227000 |
| C | 0.984199000 | 1.917617000 | 6.491503000 |
| C | 2.274754000 | 2.023574000 | 7.025435000 |

| | | | |
|---|---|---|---|
| H | 11.066263000 | 0.811382000 | 6.623889000 |
| H | 11.201660000 | -0.943960000 | 6.945794000 |
| H | 10.360436000 | 0.140036000 | 8.104423000 |
| H | 6.756526000 | 0.198792000 | 8.578911000 |
| H | 8.422931000 | -0.299041000 | 8.984171000 |
| H | 7.181597000 | -1.533695000 | 8.612999000 |
| H | 9.875694000 | 0.022881000 | 2.890871000 |
| H | 10.688566000 | -1.339374000 | 3.711868000 |
| H | 11.028819000 | 0.337785000 | 4.223615000 |
| H | 7.528368000 | -0.261473000 | 2.454460000 |
| H | 6.089765000 | -1.016250000 | 3.164517000 |
| H | 7.547727000 | -2.009932000 | 2.831992000 |
| H | 5.004735000 | -1.189540000 | 5.062140000 |
| H | 5.025465000 | -0.225507000 | 6.567797000 |
| H | 5.415301000 | -1.968565000 | 6.621085000 |
| H | 7.785646000 | 5.355312000 | 8.015620000 |
| H | 8.460037000 | 7.704436000 | 8.585859000 |
| H | 9.565221000 | 9.142907000 | 6.847706000 |
| H | 9.985531000 | 8.217115000 | 4.552406000 |
| H | 9.297192000 | 5.879417000 | 3.999760000 |
| H | 4.822205000 | 8.112339000 | 2.207336000 |
| H | 6.478318000 | 6.749218000 | 0.904881000 |
| H | 7.586484000 | 4.777496000 | 1.963260000 |
| H | 5.395480000 | 5.487408000 | 5.624684000 |
| H | 4.285693000 | 7.480574000 | 4.581027000 |
| H | 4.235136000 | 1.015856000 | 9.460462000 |
| H | 4.529116000 | 0.708203000 | 11.926355000 |
| H | 6.027883000 | 2.255232000 | 13.217293000 |
| H | 7.222878000 | 4.114400000 | 12.021257000 |
| H | 6.938784000 | 4.400916000 | 9.554562000 |
| H | 11.965699000 | 3.220293000 | 10.588272000 |
| H | 9.714280000 | 2.121389000 | 10.862314000 |
| H | 8.137156000 | 2.020106000 | 8.933325000 |
| H | 10.978675000 | 4.143711000 | 6.460767000 |
| H | 12.580073000 | 4.233441000 | 8.372521000 |
| H | 2.517424000 | 1.558280000 | 7.992116000 |
| H | 0.208917000 | 1.362491000 | 7.042000000 |
| H | -0.337949000 | 2.434454000 | 4.839681000 |
| H | 1.438521000 | 3.700182000 | 3.591904000 |
| H | 3.749996000 | 3.868469000 | 4.535040000 |
| H | 4.491149000 | 1.113296000 | 4.671529000 |
| H | 2.929127000 | 0.231894000 | 2.945706000 |
| H | 3.417621000 | 0.596062000 | 0.500579000 |
| H | 5.483406000 | 1.865016000 | -0.163615000 |
| H | 7.032698000 | 2.738584000 | 1.576316000 |

**$[Ni_4Ga_4](Cp^*)_4(hex)_2$**

| | | | |
|---|---|---|---|
| Ni | 1.591439000 | -0.272510000 | 1.317426000 |
| Ni | -0.739566000 | -0.351635000 | 1.687923000 |
| H | 1.076730000 | 4.395829000 | 4.509109000 |
| C | 0.234875000 | 4.814786000 | 3.923261000 |
| H | 0.323495000 | 5.922509000 | 3.973325000 |
| H | -0.708479000 | 4.555604000 | 4.449611000 |
| C | 0.241961000 | 4.334153000 | 2.502316000 |
| C | 1.201887000 | 3.549848000 | 1.878207000 |
| C | 2.464128000 | 2.987247000 | 2.454224000 |
| H | 2.458390000 | 2.991861000 | 3.562281000 |
| H | 3.366235000 | 3.553367000 | 2.128235000 |
| H | 2.606882000 | 1.927791000 | 2.134110000 |
| C | 0.803181000 | 3.371610000 | 0.456638000 |
| C | 1.898656000 | 3.495090000 | -0.599217000 |
| H | 2.683199000 | 2.722677000 | -0.465215000 |
| H | 2.388000000 | 4.492316000 | -0.541425000 |
| H | 1.503906000 | 3.372611000 | -1.625580000 |
| C | -0.463253000 | 4.140531000 | 0.296750000 |
| C | -1.202474000 | 4.270939000 | -1.002636000 |
| H | -1.549089000 | 3.286468000 | -1.388278000 |
| H | -2.099519000 | 4.912432000 | -0.900587000 |
| H | -0.567396000 | 4.717877000 | -1.799504000 |
| Ga | 0.148353000 | 1.409539000 | 0.404188000 |
| C | -0.795380000 | 4.685693000 | 1.531448000 |
| C | -1.990389000 | 5.522866000 | 1.882833000 |

| | | | |
|---|---|---|---|
| H | -2.598960000 | 5.058762000 | 2.689386000 |
| H | -1.686239000 | 6.523927000 | 2.259605000 |
| H | -2.658905000 | 5.684122000 | 1.015082000 |
| H | 5.352856000 | -3.219117000 | 0.931998000 |
| C | 5.402306000 | -2.268347000 | 1.496338000 |
| H | 6.322528000 | -2.299355000 | 2.118229000 |
| H | 4.539361000 | -2.248249000 | 2.196259000 |
| C | 5.397764000 | -1.075066000 | 0.586089000 |
| C | 5.408690000 | -1.066054000 | -0.852116000 |
| C | 5.527561000 | -2.246535000 | -1.771119000 |
| H | 5.355957000 | -3.201486000 | -1.240156000 |
| H | 6.541583000 | -2.296539000 | -2.223910000 |
| H | 4.801055000 | -2.196386000 | -2.608089000 |
| C | 5.380879000 | 0.312374000 | -1.286227000 |
| C | 5.443572000 | 0.775436000 | -2.712005000 |
| H | 4.893472000 | 0.091339000 | -3.388367000 |
| H | 6.493044000 | 0.826364000 | -3.076919000 |
| H | 5.003410000 | 1.784352000 | -2.835254000 |
| C | 5.368855000 | 1.149127000 | -0.111665000 |
| C | 5.446272000 | 2.647472000 | -0.102410000 |
| H | 5.030181000 | 3.086775000 | -1.029509000 |
| H | 4.890007000 | 3.085020000 | 0.748627000 |
| H | 6.500616000 | 2.991048000 | -0.021240000 |
| Ga | 3.367399000 | -0.104371000 | -0.202148000 |
| C | 5.368560000 | 0.288929000 | 1.042427000 |
| C | 5.342669000 | 0.703675000 | 2.484497000 |
| H | 4.490298000 | 0.238595000 | 3.024090000 |
| H | 6.273604000 | 0.398063000 | 3.008798000 |
| H | 5.242385000 | 1.799629000 | 2.592977000 |
| H | -5.217785000 | -2.314141000 | 2.408095000 |
| C | -5.654400000 | -2.091300000 | 1.413596000 |
| H | -6.760189000 | -2.099122000 | 1.534144000 |
| H | -5.389629000 | -2.931744000 | 0.742186000 |
| C | -5.166225000 | -0.776440000 | 0.876651000 |
| C | -4.929980000 | 0.411724000 | 1.673941000 |
| C | -5.203352000 | 0.515211000 | 3.146347000 |
| H | -4.711015000 | -0.294614000 | 3.723553000 |
| H | -6.293785000 | 0.445273000 | 3.351942000 |
| H | -4.850637000 | 1.478049000 | 3.560817000 |
| C | -4.540721000 | 1.473964000 | 0.778234000 |
| C | -4.167145000 | 2.879745000 | 1.150246000 |
| H | -4.299408000 | 3.063082000 | 2.233027000 |
| H | -4.791048000 | 3.621861000 | 0.609016000 |
| H | -3.106518000 | 3.102343000 | 0.910221000 |
| C | -4.545453000 | 0.946486000 | -0.558505000 |
| C | -4.156447000 | 1.689844000 | -1.804386000 |
| H | -4.198992000 | 2.785756000 | -1.653392000 |
| H | -3.117475000 | 1.436908000 | -2.113414000 |
| H | -4.825825000 | 1.437709000 | -2.652429000 |
| Ga | -2.897941000 | -0.214342000 | 0.789649000 |
| C | -4.945957000 | -0.432358000 | -0.499920000 |
| C | -5.086216000 | -1.334586000 | -1.688687000 |
| H | -5.373876000 | -2.361812000 | -1.394620000 |
| H | -5.864540000 | -0.958415000 | -2.387069000 |
| H | -4.138185000 | -1.400019000 | -2.257617000 |
| H | 3.266049000 | -3.503082000 | 0.030503000 |
| C | 2.605860000 | -3.972321000 | -0.724832000 |
| H | 2.977241000 | -5.006819000 | -0.898001000 |
| H | 2.738898000 | -3.406999000 | -1.667228000 |
| C | 1.175412000 | -3.954029000 | -0.278542000 |
| C | 0.700099000 | -4.164998000 | 1.068754000 |
| C | 1.586629000 | -4.431696000 | 2.246743000 |
| H | 2.498643000 | -3.800941000 | 2.219624000 |
| H | 1.926722000 | -5.490543000 | 2.263653000 |
| H | 1.072106000 | -4.235166000 | 3.205706000 |
| C | -0.733507000 | -4.141815000 | 1.037740000 |
| C | -1.676003000 | -4.229308000 | 2.201874000 |
| H | -1.134976000 | -4.322353000 | 3.163116000 |
| H | -2.354814000 | -5.105088000 | 2.116053000 |
| H | -2.317850000 | -3.323649000 | 2.268672000 |
| C | -1.152308000 | -3.947058000 | -0.322860000 |
| C | -2.579052000 | -3.798630000 | -0.751558000 |
| H | -3.036572000 | -2.894688000 | -0.293388000 |

| | | | |
|---|---|---|---|
| H | -2.669260000 | -3.680833000 | -1.847996000 |
| H | -3.193513000 | -4.673709000 | -0.450796000 |
| Ga | 0.238094000 | -1.976254000 | 0.240257000 |
| C | 0.018823000 | -3.838799000 | -1.143530000 |
| C | 0.084500000 | -3.709166000 | -2.634966000 |
| H | 0.688676000 | -2.832434000 | -2.947952000 |
| H | 0.535490000 | -4.612675000 | -3.098617000 |
| C | 1.549701000 | -1.384526000 | 4.123349000 |
| H | 2.227137000 | -2.106056000 | 3.626639000 |
| H | 2.203136000 | -0.746530000 | 4.762582000 |
| C | 0.528037000 | -2.130763000 | 4.991846000 |
| H | -0.164377000 | -2.715686000 | 4.353511000 |
| H | 1.023242000 | -2.825142000 | 5.701589000 |
| H | -0.093462000 | -1.424646000 | 5.578523000 |
| C | 0.902920000 | -0.473516000 | 3.104637000 |
| C | -0.080313000 | 0.427355000 | 3.250865000 |
| C | -0.558421000 | 1.398255000 | 4.273661000 |
| C | -1.903120000 | 2.040797000 | 3.947445000 |
| H | -2.669731000 | 1.258897000 | 3.791088000 |
| H | -2.246049000 | 2.718304000 | 4.755897000 |
| H | -1.824428000 | 2.618991000 | 3.005690000 |
| H | -0.612062000 | 0.848373000 | 5.243715000 |
| H | 0.222313000 | 2.174910000 | 4.418050000 |
| H | -0.922879000 | -3.578213000 | -3.069645000 |
| C | -0.114602000 | 0.327207000 | -2.470887000 |
| C | 0.297918000 | 1.522305000 | -3.311538000 |
| H | -0.381052000 | 1.611900000 | -4.189125000 |
| C | 1.759227000 | 1.474165000 | -3.772374000 |
| H | 2.037340000 | 2.372590000 | -4.362410000 |
| H | 1.946860000 | 0.575696000 | -4.395372000 |
| H | 2.429137000 | 1.403998000 | -2.889675000 |
| H | 0.128957000 | 2.441991000 | -2.713645000 |
| C | -1.146534000 | -0.521628000 | -2.606849000 |
| C | -1.937916000 | -1.049432000 | -3.756351000 |
| H | -2.801900000 | -0.355877000 | -3.887652000 |
| C | -1.168098000 | -1.185617000 | -5.078667000 |
| H | -1.811111000 | -1.606679000 | -5.878717000 |
| H | -0.788716000 | -0.205394000 | -5.428771000 |
| H | -0.291842000 | -1.853064000 | -4.955130000 |
| H | -2.408184000 | -2.018614000 | -3.482591000 |
| Ni | -1.118861000 | -0.213369000 | -0.756657000 |
| Ni | 1.212073000 | -0.207789000 | -1.098726000 |

**$[Ni_5Ga_3](Cp^*)_3(hex)_4$**

| | | | |
|---|---|---|---|
| Ni | 1.868891000 | 5.420699000 | 27.825889000 |
| Ni | 2.794290000 | 2.846849000 | 27.621079000 |
| Ni | 5.526411000 | 3.029688000 | 28.367486000 |
| Ni | 3.386124000 | 4.258709000 | 29.868908000 |
| Ni | 4.355630000 | 4.939522000 | 26.677399000 |
| Ga | 4.225574000 | 6.242766000 | 28.802086000 |
| Ga | 4.193423000 | 1.047312000 | 27.882227000 |
| C | 2.633450000 | 8.316135000 | 29.825420000 |
| C | 4.018084000 | 8.373693000 | 30.073554000 |
| C | 4.697865000 | 8.454698000 | 28.787068000 |
| C | 3.672659000 | 8.514522000 | 27.765747000 |
| C | 2.419300000 | 8.374011000 | 28.403995000 |
| C | 1.553208000 | 8.266742000 | 30.857860000 |
| H | 1.158517000 | 9.274936000 | 31.069452000 |
| H | 1.918351000 | 7.858159000 | 31.808561000 |
| H | 0.704185000 | 7.651007000 | 30.535321000 |
| C | 4.685793000 | 8.412591000 | 31.413427000 |
| H | 4.723622000 | 9.436141000 | 31.821530000 |
| H | 5.721563000 | 8.050740000 | 31.360919000 |
| H | 4.155230000 | 7.789560000 | 32.147447000 |
| C | 6.115489000 | 8.916212000 | 28.597993000 |
| H | 6.180488000 | 10.013721000 | 28.683263000 |
| H | 6.505086000 | 8.642357000 | 27.609915000 |
| H | 6.795673000 | 8.497992000 | 29.352392000 |
| C | 3.932385000 | 8.643144000 | 26.298856000 |
| H | 4.753603000 | 9.344972000 | 26.094343000 |
| H | 3.044263000 | 9.011323000 | 25.768903000 |
| H | 4.197197000 | 7.671497000 | 25.847886000 |

| | | | |
|---|---|---|---|
| C | 1.072575000 | 8.321859000 | 27.740409000 |
| H | 0.354699000 | 8.998976000 | 28.227372000 |
| H | 0.605717000 | 7.310526000 | 27.772532000 |
| H | 1.133738000 | 8.593984000 | 26.679594000 |
| C | 3.166283000 | -1.261010000 | 28.127534000 |
| C | 4.600614000 | -1.146661000 | 28.080586000 |
| C | 4.963402000 | -0.788639000 | 26.718833000 |
| C | 3.755068000 | -0.653530000 | 25.973940000 |
| C | 2.657619000 | -0.951949000 | 26.837341000 |
| C | 2.374654000 | -1.678187000 | 29.328133000 |
| H | 2.292765000 | -2.775229000 | 29.394853000 |
| H | 1.354735000 | -1.274575000 | 29.302786000 |
| H | 2.840336000 | -1.334054000 | 30.262126000 |
| C | 5.562897000 | -1.553371000 | 29.154705000 |
| H | 5.915778000 | -2.588167000 | 29.013225000 |
| H | 5.104400000 | -1.495303000 | 30.150838000 |
| H | 6.447741000 | -0.899866000 | 29.166239000 |
| C | 6.362394000 | -0.734989000 | 26.191992000 |
| H | 6.798969000 | -1.743661000 | 26.119393000 |
| H | 7.019688000 | -0.140732000 | 26.843584000 |
| H | 6.399949000 | -0.284132000 | 25.192905000 |
| C | 3.623256000 | -0.246798000 | 24.538914000 |
| H | 4.580106000 | 0.090838000 | 24.121366000 |
| H | 2.902199000 | 0.575693000 | 24.419085000 |
| H | 3.267513000 | -1.081548000 | 23.914158000 |
| C | 1.222956000 | -0.929544000 | 26.411886000 |
| H | 1.015578000 | -1.715053000 | 25.667620000 |
| H | 0.952003000 | 0.030182000 | 25.944707000 |
| H | 0.543703000 | -1.091148000 | 27.256998000 |
| C | 0.734513000 | 4.914807000 | 31.728554000 |
| C | 0.244304000 | 4.837493000 | 30.275948000 |
| C | 1.335867000 | 4.355851000 | 29.326666000 |
| C | 1.252131000 | 1.852253000 | 29.934885000 |
| C | 1.848000000 | 3.086695000 | 29.310348000 |
| C | 0.047430000 | 1.338304000 | 29.138645000 |
| H | -0.618173000 | 4.152124000 | 30.206922000 |
| H | -0.126499000 | 5.824847000 | 29.967583000 |
| H | 0.993525000 | 3.920332000 | 32.114056000 |
| H | -0.031389000 | 5.351888000 | 32.385949000 |
| H | 1.641714000 | 5.530895000 | 31.785537000 |
| H | -0.397698000 | 0.449708000 | 29.609632000 |
| H | 0.356839000 | 1.071466000 | 28.119859000 |
| H | -0.731095000 | 2.108052000 | 29.056858000 |
| H | 2.002125000 | 1.054220000 | 30.010486000 |
| H | 0.938453000 | 2.092721000 | 30.966393000 |
| C | 4.385505000 | 3.041443000 | 30.891218000 |
| C | 4.256787000 | 1.704883000 | 31.511029000 |
| H | 3.956735000 | 0.978684000 | 30.737042000 |
| H | 3.421668000 | 1.723500000 | 32.230240000 |
| C | 5.547498000 | 1.232238000 | 32.186930000 |
| H | 6.361268000 | 1.191544000 | 31.449517000 |
| H | 5.849958000 | 1.918777000 | 32.989068000 |
| H | 5.426586000 | 0.229057000 | 32.618847000 |
| C | 5.104282000 | 4.114391000 | 30.757548000 |
| C | 6.294163000 | 4.798034000 | 31.340229000 |
| H | 5.935024000 | 5.488761000 | 32.120711000 |
| H | 6.913808000 | 4.042265000 | 31.849578000 |
| C | 7.149145000 | 5.565772000 | 30.341973000 |
| H | 6.556898000 | 6.356510000 | 29.857145000 |
| H | 8.011349000 | 6.043523000 | 30.828090000 |
| H | 7.501474000 | 4.893361000 | 29.549031000 |
| Ga | 7.421016000 | 1.853383000 | 28.883308000 |
| C | 9.101484000 | 0.627541000 | 30.081294000 |
| C | 8.819827000 | -0.361357000 | 31.170023000 |
| H | 8.408238000 | 0.123815000 | 32.063734000 |
| H | 9.741480000 | -0.882098000 | 31.476788000 |
| H | 8.104858000 | -1.131263000 | 30.850472000 |
| C | 9.393275000 | 2.019259000 | 30.253647000 |
| C | 9.440552000 | 2.748886000 | 31.559905000 |
| H | 8.677996000 | 2.382402000 | 32.260294000 |
| H | 10.419101000 | 2.620708000 | 32.050062000 |
| H | 9.282611000 | 3.826402000 | 31.427716000 |
| C | 9.728156000 | 2.562866000 | 28.971700000 |

| | | | |
|---|---|---|---|
| C | 9.633325000 | 1.512123000 | 28.004263000 |
| C | 9.935732000 | 1.634544000 | 26.541741000 |
| H | 9.378196000 | 0.896142000 | 25.950265000 |
| H | 11.006497000 | 1.477477000 | 26.335289000 |
| H | 9.672779000 | 2.629047000 | 26.156927000 |
| C | 10.211278000 | 3.953744000 | 28.705185000 |
| H | 9.733739000 | 4.692532000 | 29.360257000 |
| H | 11.298802000 | 4.027524000 | 28.867228000 |
| H | 10.020703000 | 4.256397000 | 27.667615000 |
| C | 9.264469000 | 0.310245000 | 28.691988000 |
| C | 9.253556000 | -1.071324000 | 28.115785000 |
| H | 8.439034000 | -1.688652000 | 28.516149000 |
| H | 10.197189000 | -1.589221000 | 28.352432000 |
| H | 9.156249000 | -1.057979000 | 27.024128000 |
| C | 1.919715000 | 4.429103000 | 26.132037000 |
| C | 2.855847000 | 5.171418000 | 25.530676000 |
| C | 2.909400000 | 5.742985000 | 24.141235000 |
| C | 1.710515000 | 6.655963000 | 23.847446000 |
| H | 0.767240000 | 6.101786000 | 23.939464000 |
| H | 1.678052000 | 7.484897000 | 24.566283000 |
| H | 1.769986000 | 7.077025000 | 22.833878000 |
| H | 2.913919000 | 4.901273000 | 23.423450000 |
| H | 3.848468000 | 6.290771000 | 23.979940000 |
| C | 0.897261000 | 3.417390000 | 25.680479000 |
| H | 1.001406000 | 3.238718000 | 24.595844000 |
| H | 1.130489000 | 2.435683000 | 26.167034000 |
| C | -0.538731000 | 3.794292000 | 26.049862000 |
| H | -0.836590000 | 4.725805000 | 25.549754000 |
| H | -1.244532000 | 3.001758000 | 25.764532000 |
| H | -0.607904000 | 3.961485000 | 27.133342000 |
| C | 6.145774000 | 2.739522000 | 25.368687000 |
| C | 6.166710000 | 3.385993000 | 23.980179000 |
| H | 5.214217000 | 3.895838000 | 23.785862000 |
| H | 6.967635000 | 4.133141000 | 23.903285000 |
| H | 6.324960000 | 2.630136000 | 23.197901000 |
| H | 5.379228000 | 1.952656000 | 25.403210000 |
| H | 7.106347000 | 2.235756000 | 25.573951000 |
| C | 5.887381000 | 3.722079000 | 26.469155000 |
| C | 6.251405000 | 4.937289000 | 26.837910000 |
| C | 7.391299000 | 5.883922000 | 26.899808000 |
| H | 7.319527000 | 6.519913000 | 27.791630000 |
| H | 8.333711000 | 5.319753000 | 26.989986000 |
| C | 7.436944000 | 6.785394000 | 25.655048000 |
| H | 6.498400000 | 7.345741000 | 25.556884000 |
| H | 8.269162000 | 7.500153000 | 25.724542000 |
| H | 7.566213000 | 6.191226000 | 24.741360000 |

**$[Ni_8Ga_6](Cp^*)_6$**

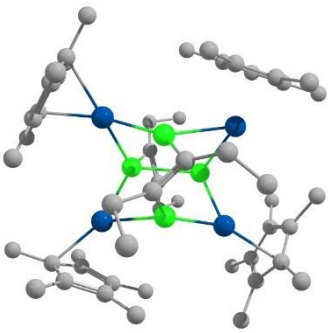
| | | | |
|---|---|---|---|
| Ga | 1.790540000 | 4.481734000 | 3.680842000 |
| Ni | 2.180096000 | 2.025592000 | 3.520440000 |
| Ga | 0.051594000 | 5.836996000 | 5.102473000 |
| Ga | -0.110270000 | 2.707048000 | 3.716638000 |
| Ni | 2.455577000 | 6.081313000 | 5.340459000 |
| Ni | -0.406298000 | 4.963199000 | 2.921851000 |
| Ni | 2.658931000 | 3.552207000 | 5.580533000 |
| Ga | -0.488353000 | 3.043380000 | 7.074190000 |
| Ni | -0.886228000 | 5.497997000 | 7.235110000 |
| Ga | 1.266932000 | 1.707148000 | 5.662219000 |
| Ga | 1.407905000 | 4.825128000 | 7.052341000 |
| Ni | -1.153544000 | 1.453349000 | 5.433456000 |
| Ni | 1.720486000 | 2.580162000 | 7.838367000 |
| Ni | -1.346077000 | 4.004909000 | 5.176590000 |
| H | 5.891156000 | 5.861955000 | 4.096929000 |
| H | 5.767107000 | 5.852585000 | 6.551003000 |
| C | 5.293075000 | 6.647422000 | 3.596055000 |
| H | 5.989972000 | 7.478615000 | 3.344842000 |
| H | 4.927107000 | 6.228294000 | 2.638497000 |
| C | 5.429338000 | 6.894035000 | 6.728226000 |
| H | 6.289517000 | 7.559607000 | 6.494419000 |
| H | 5.223970000 | 6.997032000 | 7.810170000 |
| C | 4.169145000 | 7.124031000 | 4.463552000 |
| C | 4.231062000 | 7.245526000 | 5.897709000 |

| | | | |
|---|---|---|---|
| H | 3.074137000 | 7.221405000 | 1.908174000 |
| C | 2.916811000 | 7.677578000 | 4.016302000 |
| C | 2.446306000 | 7.813749000 | 2.601920000 |
| C | 3.013740000 | 7.874610000 | 6.347849000 |
| H | 3.280539000 | 7.724433000 | 8.492449000 |
| H | 2.465328000 | 8.869671000 | 2.253859000 |
| C | 2.195212000 | 8.144104000 | 5.183785000 |
| C | 2.669971000 | 8.274416000 | 7.750509000 |
| H | 1.410902000 | 7.432969000 | 2.496853000 |
| H | 2.825736000 | 9.362210000 | 7.925716000 |
| H | 1.608175000 | 8.048665000 | 7.968904000 |
| C | 0.929649000 | 8.952664000 | 5.167961000 |
| H | 0.348512000 | 8.767765000 | 4.243008000 |
| H | 0.274235000 | 8.708981000 | 6.026455000 |
| H | 1.143377000 | 10.044220000 | 5.210399000 |
| C | 2.270740000 | 1.552662000 | 1.468634000 |
| C | 1.162486000 | 1.587616000 | 0.460044000 |
| H | 0.661441000 | 2.573680000 | 0.466010000 |
| H | 1.537844000 | 1.408237000 | -0.572373000 |
| H | 0.392788000 | 0.819847000 | 0.672263000 |
| C | 2.722478000 | 0.398735000 | 2.213165000 |
| C | 3.894630000 | 0.785973000 | 2.959416000 |
| C | 4.180465000 | 2.165824000 | 2.665623000 |
| C | 5.346891000 | 2.963424000 | 3.163677000 |
| H | 5.020165000 | 3.947136000 | 3.552572000 |
| H | 5.871023000 | 2.443612000 | 3.987931000 |
| H | 6.093306000 | 3.145880000 | 2.359576000 |
| C | 4.751135000 | -0.140088000 | 3.768897000 |
| H | 5.303352000 | 0.397845000 | 4.563947000 |
| H | 5.510345000 | -0.648723000 | 3.133235000 |
| H | 4.151837000 | -0.931488000 | 4.259728000 |
| C | 2.233582000 | -1.007008000 | 2.035763000 |
| H | 1.142997000 | -1.054964000 | 1.855052000 |
| H | 2.729523000 | -1.488481000 | 1.162678000 |
| H | 2.452557000 | -1.637500000 | 2.919017000 |
| C | 3.189060000 | 2.639204000 | 1.728010000 |
| C | 3.200613000 | 3.961849000 | 1.017819000 |
| H | 3.675206000 | 3.881495000 | 0.014343000 |
| H | 2.176189000 | 4.364547000 | 0.872826000 |
| H | 3.773705000 | 4.721376000 | 1.588041000 |
| C | -4.212560000 | 0.730026000 | 4.234810000 |
| H | -4.678276000 | 1.608349000 | 4.725271000 |
| H | -4.971784000 | -0.084032000 | 4.234709000 |
| H | -4.025850000 | 1.000221000 | 3.177750000 |
| C | -2.955342000 | 0.314633000 | 4.937571000 |
| C | -2.769514000 | 0.322555000 | 6.366901000 |
| C | -3.812081000 | 0.690038000 | 7.378079000 |
| H | -4.430593000 | -0.193666000 | 7.653967000 |
| H | -4.503821000 | 1.463437000 | 6.993434000 |
| H | -3.363903000 | 1.078648000 | 8.313605000 |
| C | -1.475825000 | -0.245021000 | 6.655479000 |
| C | -0.862118000 | -0.618691000 | 5.398353000 |
| C | 0.416271000 | -1.386630000 | 5.229993000 |
| H | 1.024579000 | -0.984310000 | 4.397128000 |
| H | 1.038306000 | -1.336306000 | 6.145682000 |
| H | 0.223435000 | -2.462189000 | 5.019327000 |
| C | -0.882077000 | -0.473204000 | 8.009640000 |
| H | -1.401851000 | 0.123492000 | 8.784537000 |
| H | 0.176983000 | -0.151020000 | 8.029505000 |
| H | -0.928908000 | -1.541057000 | 8.316602000 |
| C | -1.781347000 | -0.271340000 | 4.335970000 |
| C | -1.571292000 | -0.586673000 | 2.884710000 |
| H | -2.296225000 | -0.054552000 | 2.239860000 |
| H | -1.680957000 | -1.674965000 | 2.680398000 |
| H | -0.555769000 | -0.288293000 | 2.556902000 |
| C | -1.767345000 | 4.976002000 | 9.111567000 |
| C | -2.838261000 | 5.254447000 | 8.186774000 |
| C | -3.931260000 | 4.303225000 | 7.805672000 |
| H | -4.622611000 | 4.106164000 | 8.654044000 |
| H | -4.538033000 | 4.701491000 | 6.970048000 |
| H | -3.516905000 | 3.333011000 | 7.470012000 |
| C | -2.706921000 | 6.617750000 | 7.745664000 |
| C | -1.551128000 | 7.192231000 | 8.388683000 |

| | | | |
|---|---|---|---|
| C | -1.185180000 | 8.645750000 | 8.369990000 |
| H | -1.430315000 | 9.120823000 | 7.399725000 |
| H | -1.737879000 | 9.207479000 | 9.156627000 |
| H | -0.106617000 | 8.807493000 | 8.555377000 |
| C | -3.699428000 | 7.355960000 | 6.899660000 |
| H | -4.091786000 | 6.726700000 | 6.077370000 |
| H | -4.573216000 | 7.688285000 | 7.503618000 |
| H | -3.256393000 | 8.260930000 | 6.442063000 |
| C | -1.601412000 | 3.727799000 | 9.927573000 |
| H | -2.145476000 | 2.873260000 | 9.474823000 |
| H | -0.537182000 | 3.428069000 | 10.008007000 |
| H | -1.998827000 | 3.858456000 | 10.958780000 |
| C | -0.956044000 | 6.171801000 | 9.223049000 |
| C | 0.163538000 | 6.364788000 | 10.202756000 |
| H | 0.873944000 | 7.145321000 | 9.869493000 |
| H | 0.737158000 | 5.427897000 | 10.336214000 |
| H | -0.218252000 | 6.665836000 | 11.204118000 |
| C | 3.391706000 | 3.329584000 | 8.983234000 |
| C | 3.855211000 | 2.486118000 | 7.901401000 |
| C | 4.795564000 | 2.895020000 | 6.806791000 |
| H | 5.015094000 | 2.053667000 | 6.126332000 |
| H | 5.764348000 | 3.268450000 | 7.205954000 |
| H | 4.416594000 | 3.772537000 | 6.180590000 |
| C | 3.318794000 | 1.157165000 | 8.115276000 |
| C | 3.643878000 | -0.048117000 | 7.285308000 |
| H | 2.931475000 | -0.874133000 | 7.476404000 |
| H | 4.664945000 | -0.434309000 | 7.498601000 |
| H | 3.595391000 | 0.184879000 | 6.202394000 |
| C | 2.508516000 | 1.190559000 | 9.304036000 |
| C | 1.910818000 | 0.014700000 | 10.016436000 |
| H | 2.545499000 | -0.290549000 | 10.878584000 |
| H | 1.814939000 | -0.866618000 | 9.354404000 |
| H | 0.902939000 | 0.241183000 | 10.416576000 |
| C | 3.831036000 | 4.744095000 | 9.212125000 |
| H | 3.904418000 | 5.293983000 | 8.252767000 |
| H | 3.121817000 | 5.296066000 | 9.859371000 |
| H | 4.830941000 | 4.787982000 | 9.698627000 |
| C | 2.548750000 | 2.534594000 | 9.836834000 |
| C | 1.989851000 | 2.939886000 | 11.166914000 |
| H | 1.012160000 | 2.459553000 | 11.368243000 |
| H | 1.845028000 | 4.034802000 | 11.238899000 |
| H | 2.673202000 | 2.646506000 | 11.995516000 |
| C | -2.370867000 | 7.565778000 | 3.575580000 |
| H | -2.282491000 | 7.312795000 | 4.651053000 |
| H | -3.418418000 | 7.896005000 | 3.397964000 |
| H | -1.712280000 | 8.434178000 | 3.381968000 |
| C | -2.011582000 | 6.396201000 | 2.710828000 |
| C | -2.540747000 | 5.057439000 | 2.871226000 |
| C | -3.484237000 | 4.610691000 | 3.949226000 |
| H | -4.398193000 | 5.244487000 | 3.986207000 |
| H | -3.058889000 | 4.709551000 | 5.004224000 |
| H | -3.806297000 | 3.564094000 | 3.809575000 |
| C | -2.082687000 | 4.264386000 | 1.747596000 |
| C | -1.243780000 | 5.097728000 | 0.928319000 |
| C | -0.681902000 | 4.761097000 | -0.420811000 |
| H | 0.376684000 | 5.074340000 | -0.522463000 |
| H | -0.730810000 | 3.675789000 | -0.628788000 |
| H | -1.250799000 | 5.273631000 | -1.228486000 |
| C | -2.500743000 | 2.853262000 | 1.464326000 |
| H | -2.523225000 | 2.255143000 | 2.398610000 |
| H | -1.800240000 | 2.351064000 | 0.769909000 |
| H | -3.515622000 | 2.804976000 | 1.011448000 |
| C | -1.202426000 | 6.416559000 | 1.522330000 |
| C | -0.614135000 | 7.627249000 | 0.863239000 |
| H | -0.433552000 | 8.447249000 | 1.584482000 |
| H | -1.298839000 | 8.024308000 | 0.079851000 |
| H | 0.350083000 | 7.400827000 | 0.367865000 |

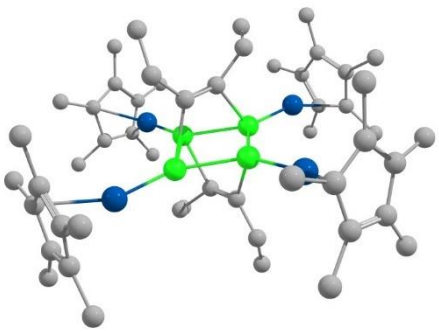
## Possible geometries of $[Ni_4Ga_4](Cp^*)_4(hex)_2$

**A**



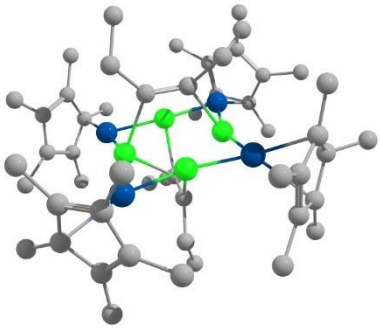
Tetrahedral $Ni_4$-core
4 $Ni_2$-edge-bridging GaCp*
2 $Ni_2$-edge-bridging hexyne (*trans*)

**B**



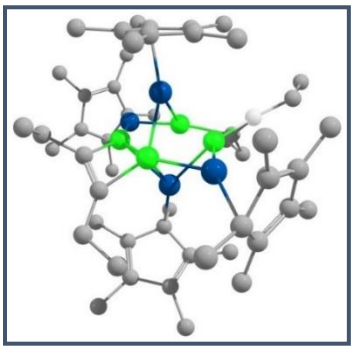
Square-planar $Ni_4$-core
4 terminal GaCp*
2 Ni-face-bridging hexyne (*trans*)

**C**



Square-planar $Ni_4$-core
4 $Ni_2$-edge-bridging GaCp*
2 Ni-face-bridging hexyne (*trans*)

**D**



Square-planar $Ni_4$-core
2 $Ni_2$-edge-bridging GaCp*
2 $Ni_4$-face-bridging GaCp*
2 $Ni_2$-edge-bridging hexyne (*trans*)

Above, four possible geometries of **3** were depicted resulting in a minimum of structures A and D. Structures B and C could not be optimized to a local minimum. Regarding the analytical results, especially the NMR data, only D remains as possible structure for **3** due to two different GaCp* bonding.

## References


[1] D. J. Krysan, P. B. Mackenzie, *J. Org. Chem.* **1990**, *55*, 4229-4230.
[2] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305-1314.
[3] C. Ganesamoorthy, S. Loerke, C. Gemel, P. Jerabek, M. Winter, G. Frenking, R. A. Fischer, *Chem. Commun.* **2013**, *49*, 2858-2860.
[4] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73-78.
[5] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.
[6] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822-8824.
[7] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.
[8] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys* **2005**, *7*, 3297-3305.
[9] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *J. Chem. Phys.* **2009**, *356*, 98-109.